

CONTENTS

1. Introduction	...1
2. Preparation Methods and Characterization Techniques	...5
3. Objectives	...21
6. Results and Discussion	...21
7. Significance of the Green Synthesis Method	...21
7. Conclusion	...22

DEPARTMENT OF PHYSICS

A STUDY PROJECT ON THE CHARACTERIZATION TECHNIQUES USED TO KNOW THE CRYSTAL STRUCTURE AND MORPHOLOGY OF THE MATERIAL

THE PROJECT WORK SUBMITTED

BY

Student1

AND

Student1

B.Sc (MPCS) FINAL YEAR

**GOVERNMENT DEGREE COLLEGE, ETURNAGARAM
DISTRICT MULUGU, TELANGANA STATE-506165**

CERTIFICATE

This is to certify that the project entitled "A STUDY PROJECT ON THE CHARACTERIZATION TECHNIQUES USED TO KNOW THE CRYSTAL STRUCTURE AND MORPHOLOGY OF THE MATERIAL" presented by Student 1 and Student 2 students of B.Sc(MPCS)-III year, Government Degree College, Eturnagaram is worthy of consideration for the study project to submit to Yunvatarangm student project competition, a record of this project work carried out under my guidance.

D.NAVEEN

Lecturer in Physics

Department of Physics

Govt.Degree College, Eturnagaram

Dist.; Mulugu

ACKNOWLEDGEMENT BY THE STUDENTS

This Project work would not have been possible without the help of lecturers, principal and commissioner of higher education. First we would like to express my deep sense of gratitude to my supervisor **D.Naveen** for his guidance and continuous support. to Sri A.Sanjeeva Reddy Incharge Dept.of Physics and R.Kedarishwar , Asst.Prof.of Physics, Government Degree College, .

We also gratefully thank to sri **A.Sanjeeva Reddy**, Head of the Department of Physics, **R.Kedarishwar**, Asst.Prof.of Physics, for providing necessary facilities during the project work.

We would like to thank all the lecturers of Govt.Degree College, Eturnagaram. My special thanks to my classmates and friends who helped us during project. like thank to

We also extended our thanks to **Dr.B.Ramulu, Principal**, Govt.Degree College, Eturnagaram. Finally, and most importantly we thank to Commissioner of Collegiate Education **Sri.Navin mittal** sir for providing us this opportunity.

A STUDY PROJECT ON THE CHARACTERIZATION TECHNIQUES USED TO KNOW THE CRYSTAL STRUCTURE AND MORPHOLOGY OF THE MATERIAL

Abstract:

The powerfull characterization techniques used to know the crystal structures and morphology of the material are discussed briefly in this study project.

CHARACTERIZATION TECHNIQUES

There are two characterization techniques one is microscopy and other is the spectroscopy are used to explore the nature of the nanostructures.

1. X-ray diffraction (XRD) :

X-ray diffraction by the polycrystalline samples is one of the important, powerful and widely used analytical techniques available to material scientists. For most crystalline substances of technological importance, the bulk properties of a powder or a solid polycrystalline, averaged throughout the sample are required; in general a single crystal data, even if they can be obtained, are usually of little importance except for the determination of the crystalline structure or for studying some other fundamental physical properties. X-rays can be diffracted by the crystals just in the same way as the visible light is diffracted by a diffraction grating. Intensities of diffracted beams and their directions are related to the atomic arrangements in crystals. Thus measurements of their intensities and directions would provide the desired information about the crystals. When an atom of a crystal is exposed to monochromatic beam of x-rays, the electric field vector of the radiation forces its electrons to carryout harmonic

vibrations of a frequency equal to that of incident beam and thus to undergo acceleration. These accelerated charges in turn re-emit the radiation at the frequency of their vibration, that is, at the incident wave frequency. The emitted waves have a spherical wavefront centered about the atom. Although the individual atoms scatter (re-emit) radiation in all directions, there are only a few directions in which these wavelets reinforce each other to produce plane waves. These waves are said to be produced by diffraction and are designated as zero order, first order, and second order etc., diffracted beams.

When a collimated beam of x-rays hit the sample, this beam can be diffracted by the crystalline phases. In the specimen according to Bragg's law,

$$2d\sin\theta = n\lambda$$

Where, λ is the wavelength of radiation used, d represents the spacing between the planes of the sample and n is the order of diffraction. There are only certain directions θ in which the reflections of a given wavelength from all parallel planes add up in phase to give a strong reflected (diffracted) beam. A beam of monochromatic x-rays incident on a crystal with an arbitrary angle θ is in general not reflected. Also, because $\sin\theta \leq 1$, wavelength $\lambda \leq 2d$ are essential if Bragg reflection is to occur.

1.1.GAXRD:

It is sometimes very difficult to analyze thin films due to their small diffracting volumes, which result in low diffracted intensities compared to the substrate and background. This combination of low diffracted signal and high background make it very difficult to identify the phases present. Accordingly, special techniques must be used when analyzing thin films. The most common technique for analyzing thin films as thin as 100 \AA is to use a glancing incidence angle arrangement combined with parallel beam geometry. By increasing the path length of the incident X-ray beam through the thin film, the intensity from the thin film can be increased so that conventional phase identification analysis can be run. Glancing angle x-ray diffraction (GAXRD) is used to record the diffraction pattern in films, with minimum contribution from substrate. A parallel, monochromatic x-ray beam is made to incident on a sample surface at a fixed angle and diffraction profile is recorded by a detector. When the angle of incidence

decreases, the diffracted and scattered signals at the angle 2θ arise mainly from the limited depth from the surface.

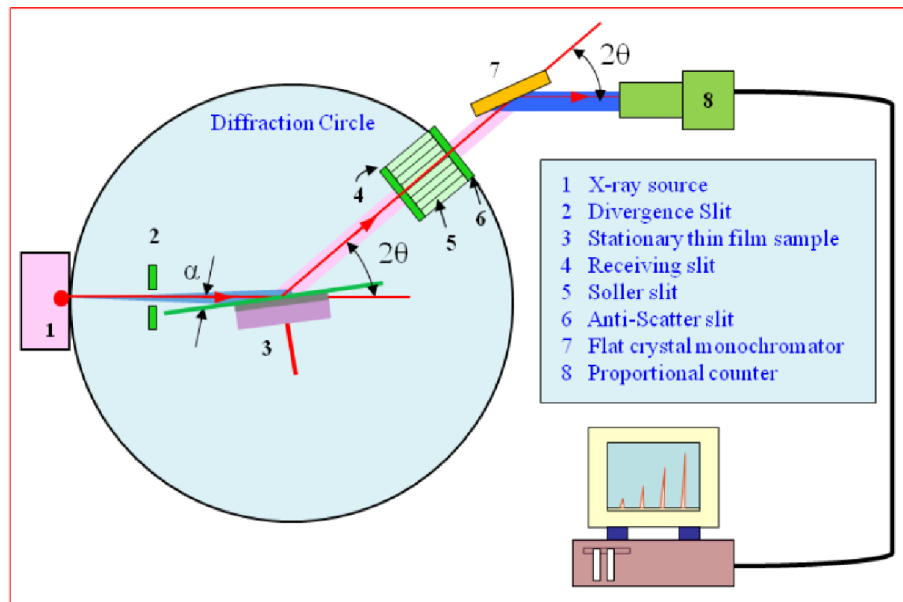


Fig. 1.1.Schematic diagram of GAXRD Technique.

This diffractometer uses $\text{CuK}\alpha$ radiation ($\lambda=1.54 \text{ \AA}$) from a rotating anode that can field a maximum power of 12kW. In this geometry, the x-rays from the source are narrowed by the incident slit and strike the sample at an angle α (glancing angle). The angle α can be varied in the range 0.5-1.00 degree.

Diffracted x-rays from the thin film sample pass through the soller slit, which limits the divergence of the x-rays in the vertical direction. After getting diffracted by the diffracted beam monochromator (graphite flat crystal), the signal is fed to a photomultiplier tube (PMT) interfaced to a computer, which stores the data in a file. The grain size can be calculated using **Debye Scherror formula** given by,

$$d = \frac{0.9\lambda}{\beta \cos \theta}$$

Where d is the average crystal size, the β full width at half maximum of the pure diffraction profile, 2θ scale in radians and λ the wavelength of the light radiation.

2. Scanning Electron Microscopy:

Scanning electron microscopy is a method for high resolution imaging of surfaces. The operation of the SEM consists of applying a voltage between a conductive sample and filament, resulting in electron emission from the filament to the sample. Electrons are generated in the electron gun. The most commonly used gun is a tungsten-hairpin gun in which a tungsten filament serves as the source of electrons. By applying a current through the filament the tungsten wire will heat up and emission of electrons can be achieved. Operation of this instrument generally occurs in the vacuum environment ranging from 10^{-4} to 10^{-10} Torr. The electrons which are emitting from the filament are guided to the sample by a series of electromagnetic lenses in the electron column.

The electrons interact with the sample within a few nanometres to several microns of the surface, depending on beam parameters and sample type. Electrons are emitted from the sample primarily as either backscattered electrons or secondary electrons. Some energy from the beam electrons is transferred to the conduction band electrons in the sample, providing enough energy for their escape from the sample surface as secondary electrons and backscattered electrons are created during e-beam solid interaction this is shown in figure 2.9. Electrons that are emitted from the sample with energies below 50 eV are called as secondary electrons while those with energies above 50 eV are called as backscattered electrons. Secondary electrons are the most common signal used for investigations of surface morphology. They are produced as a result of interactions between the beam electrons and weakly bound electrons in the conduction band of the sample. Secondary electrons are low energy electrons (50 eV), so only those formed within the first few nanometres of the sample surface have enough energy to escape and be detected. High energy beam electrons which are scattered back out of the sample (back scattered electrons) can also form secondary electrons when they leave the surface. Since these electrons travel further into the sample than the secondary electrons, they can emerge from the sample at a much larger distance away from the impact of the incident beam which makes their spatial

distribution larger. Once these electrons escape from the sample surface, they are typically detected by an Everhart-Thornely scintillator photomultiplier detector.

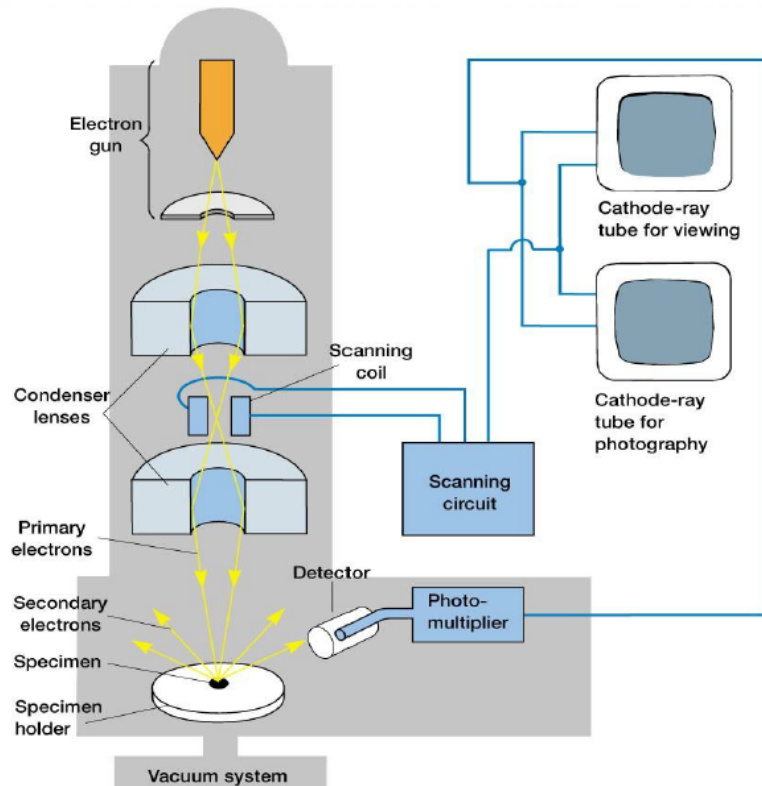


Fig.2.1 Schematic diagram for SEM .

The SEM image formed is the result of the intensity of the secondary electron emission from the sample at each x, y data point during the rastered across the sample, the emitted secondary electrons are collected by a detector, and the output can be used to modulate the brightness of a cathode ray tube(CRT) and produce corresponding image. The resolution and depth of field of the image are determined by the beam current and the final spot size, which are adjusted with one or more condenser lenses and the final, probe forming objective lenses. The schematic diagram for Scanning electron microscope is shown in the Fig.2.1. The lenses are also used to shape the beam to minimize the effects of spherical aberration, chromatic aberration, diffraction, and astigmatism. One of the key advantages of the SEM with respect to other types of

microscopy is its large depth of field. This ability makes it possible to image very rough surfaces with millimetres of vertical information within a single image. The depth of field and small beam size makes it possible to image far below the top layer. This ability also makes it possible to measure very rough surfaces over larger lateral areas as well. For scanning areas that have heights of greater than 5 to 10 μm s of variation, the SEM would be better suited for the analysis.

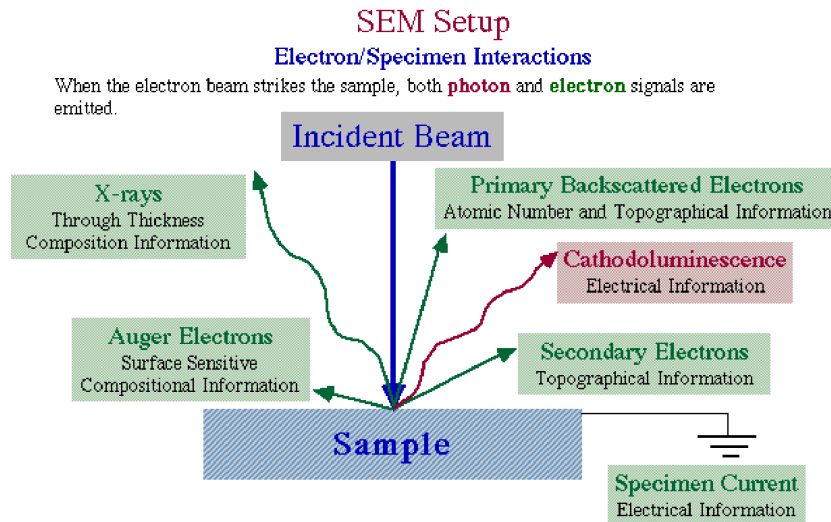


Fig 2.2.Mechanism involve in SEM.

3 Field Emission Scanning Electron Microscopy

Field emission (FE) is a physical phenomena in which, sufficiently intense electric field is applied normal to the surface of a metal or semiconductor, electrons will be emitted through the surface potential barrier into the vacuum, by the quantum mechanical tunnelling effect. The theory of field emission from metals was first derived by Fowler and Nordheim in 1928, who showed that if the temperature is not too high, most of the emitted electrons originate from a small energy interval around the Fermi level of the material. At the other extreme, high temperatures and low fields, electron emission over the potential barrier, rather than it, predominates, i.e. thermionic emission.

Study of field emission characteristics can be done by

- (1). Close proximity configuration
- (2). Conventional field emission microscope.

The field emission studies of the nanostructures have been carried out in the close proximity (CP) configuration wherein the field emitter arrays in the form of a thin film is mounted in proximity with an anode screen separated by an insulating spacer ($\sim 50 \mu\text{m}$ to a few mm). Electron tunnelling in this configuration is generally referred to as “thin-film tunnelling”. However, such a configuration poses a serious limitation on the strength of the applied electric field as relatively high field may lead to arc formation. Experimental setup of field emission shown in fig.2.10. In the case of the CP configuration, the applied field is usually calculated as $E = V/d$, where V is the applied voltage and d is the separation. This gives an average electric field and not the field at the apex of an individual emitter tip, due to the complexity posed by the large number of emitters on the cathode substrate.

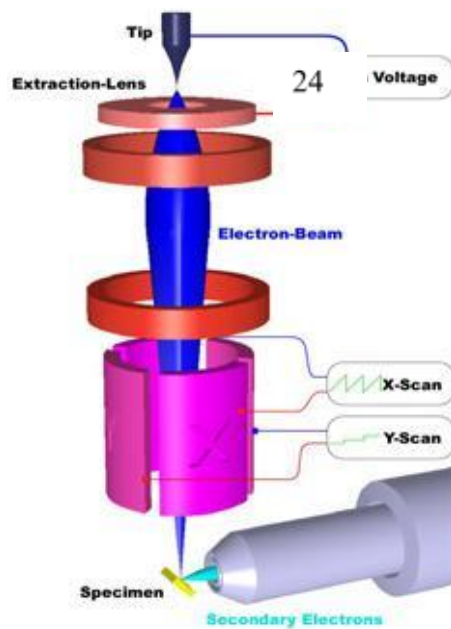


Figure 3. Schematic of a scanning electron microscope with a field emission gun column.

On the other hand, in the conventional FEM configuration, the corresponding field generated at the emitter apex is calculated using $F = \beta_0 V$, and the theoretical field enhancement factor $\beta_0 = 1/kr$, where k is a constant known as the geometrical factor and has the value 5 for a hemispherical emitter, and r is the tip radius. This field is referred to as the local field at the

emitter. As a result, comparison of field emitters is pertinent only if the field emission measurements have been carried out under the same experimental configurations. Fowler-Nordheim predicted the field emitted current density as,

$$J_{FN} = \frac{AE^2}{\phi t^2(y)} \exp \left[\frac{-Bv(y)\phi^{3/2}}{E} \right]$$

Where E is the normal component of electric field at cathode surface, ϕ is the work function where t(y) and v(y) are functions which arises due to the inclusion of image charge effects.

$$y = \left[\frac{\left(\frac{eE}{4\pi \epsilon} \right)^{1/2}}{\phi} \right]$$

4.Conclusions:

We have known from this study projet that the characterization techniques XRD (X-ray diffraction) is the most useful and important to know the crystal structure and for the confirmation of the sample. The SEM (scanning electron microscope) is a useful technique to know the morphology of the material.

References:Source: Internet

Acknowledgements:

We thank to Dr.B.Leela, Principal(FAC), Govt.Degree College, Jammikunta for giving the permission to utilize the ICT facilities in the college. We heartfully thank to sri A.Sanjeeva Reddy, Incharge, Department of Physics for his continuous encouragement in doing the projects and career guidance.

**A STUDY PROJECT ON THE CHARACTERIZATION TECHNIQUES USED TO
KNOW THE CRYSTAL STRUCTURE AND MORPHOLOGY OF THE MATERIAL**

Abstract:

The powerful characterization techniques used to know the crystal structures and morphology of the material are discussed briefly in this study project.

CHARACTERIZATION TECHNIQUES

There are two characterization techniques one is microscopy and other is the spectroscopy are used to explore the nature of the nanostructures.

1. X-ray diffraction (XRD) :

X-ray diffraction by the polycrystalline samples is one of the important, powerful and widely used analytical techniques available to material scientists. For most crystalline substances of technological importance, the bulk properties of a powder or a solid polycrystalline, averaged throughout the sample are required; in general a single crystal data, even if they can be obtained, are usually of little importance except for the determination of the crystalline structure or for studying some other fundamental physical properties. X-rays can be diffracted by the crystals just in the same way as the visible light is diffracted by a diffraction grating. Intensities of diffracted beams and their directions are related to the atomic arrangements in crystals. Thus measurements of their intensities and directions would provide the desired information about the crystals. When an atom of a crystal is exposed to monochromatic beam of x-rays, the electric field vector of the radiation forces its electrons to carry out harmonic vibrations of a frequency equal to that of incident beam and thus to undergo acceleration. These accelerated charges in turn re-emit the radiation at the frequency of their vibration, that is, at the incident wave frequency. The emitted waves have a spherical wavefront centered about the atom. Although the individual atoms scatter (re-emit) radiation in all directions, there are only a few directions in which these wavelets reinforce each other to produce plane waves. These waves are

said to be produced by diffraction and are designated as zero order, first order, and second order etc., diffracted beams.

When a collimated beam of x-rays hit the sample, this beam can be diffracted by the crystalline phases. In the specimen according to Bragg's law,

$$2d\sin\theta = n\lambda$$

Where, λ is the wavelength of radiation used, d represents the spacing between the planes of the sample and n is the order of diffraction. There are only certain directions θ in which the reflections of a given wavelength from all parallel planes add up in phase to give a strong reflected (diffracted) beam. A beam of monochromatic x-rays incident on a crystal with an arbitrary angle θ is in general not reflected. Also, because $\sin\theta \leq 1$, wavelength $\lambda \leq 2d$ are essential if Bragg reflection is to occur.

1.1.GAXRD:

It is sometimes very difficult to analyze thin films due to their small diffracting volumes, which result in low diffracted intensities compared to the substrate and background. This combination of low diffracted signal and high background make it very difficult to identify the phases present. Accordingly, special techniques must be used when analyzing thin films. The most common technique for analyzing thin films as thin as 100 \AA is to use a glancing incidence angle arrangement combined with parallel beam geometry. By increasing the path length of the incident X-ray beam through the thin film, the intensity from the thin film can be increased so that conventional phase identification analysis can be run. Glancing angle x-ray diffraction (GAXRD) is used to record the diffraction pattern¹⁹ in films, with minimum contribution from substrate. A parallel, monochromatic x-ray beam is made to incident on a sample surface at a fixed angle and diffraction profile is recorded by a detector. When the angle of incidence decreases, the diffracted and scattered signals at the angle 2θ arise mainly from the limited depth from the surface.

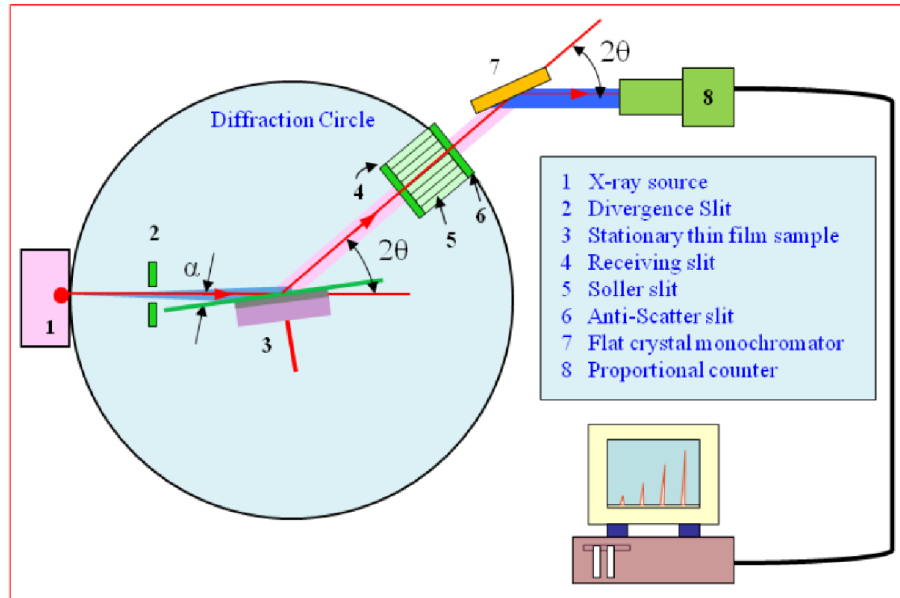


Fig. 1.1.Schematic diagram of GAXRD Technique.

This diffractometer uses $\text{CuK}\alpha$ radiation ($\lambda=1.54 \text{ \AA}$) from a rotating anode that can field a maximum power of 12kW. In this geometry, the x-rays from the source are narrowed by the incident slit and strike the sample at an angle α (glancing angle). The angle α can be varied in the range 0.5-1.00 degree.

Diffracted x-rays from the thin film sample pass through the soller slit, which limits the divergence of the x-rays in the vertical direction. After getting diffracted by the diffracted beam monochromator (graphite flat crystal), the signal is fed to a photomultiplier tube (PMT) interfaced to a computer, which stores the data in a file. The grain size can be calculated using **Debye Scherror formula** given by,

$$d = \frac{0.9\lambda}{\beta \cos \theta}$$

Where d is the average crystal size, the β full width at half maximum of the pure diffraction profile, 2θ scale in radians and λ the wavelength of the light radiation.

2. Scanning Electron Microscopy:

Scanning electron microscopy is a method for high resolution imaging of surfaces. The operation of the SEM consists of applying a voltage between a conductive sample and filament, resulting in electron emission from the filament to the sample. Electrons are generated in the electron gun. The most commonly used gun is a tungsten-hairpin gun in which a tungsten filament serves as the source of electrons. By applying a current through the filament the tungsten wire will heat up and emission of electrons can be achieved. Operation of this instrument generally occurs in the vacuum environment ranging from 10^{-4} to 10^{-10} Torr. The electrons which are emitting from the filament are guided to the sample by a series of electromagnetic lenses in the electron column.

The electrons interact with the sample within a few nanometres to several microns of the surface, depending on beam parameters and sample type. Electrons are emitted from the sample primarily as either backscattered electrons or secondary electrons. Some energy from the beam electrons is transferred to the conduction band electrons in the sample, providing enough energy for their escape from the sample surface as secondary electrons and backscattered electrons are created during e-beam solid interaction this is shown in figure 2.9. Electrons that are emitted from the sample with energies below 50 eV are called as secondary electrons while those with energies above 50 eV are called as backscattered electrons. Secondary electrons are the most common signal used for investigations of surface morphology. They are produced as a result of interactions between the beam electrons and weakly bound electrons in the conduction band of the sample. Secondary electrons are low energy electrons (50 eV), so only those formed within the first few nanometres of the sample surface have enough energy to escape and be detected. High energy beam electrons which are scattered back out of the sample (back scattered electrons) can also form secondary electrons when they leave the surface. Since these electrons travel further into the sample than the secondary electrons, they can emerge from the sample at a much larger distance away from the impact of the incident beam which makes their spatial distribution larger. Once these electrons escape from the sample surface, they are typically detected by an Everhart-Thornely scintillator photomultiplier detector.

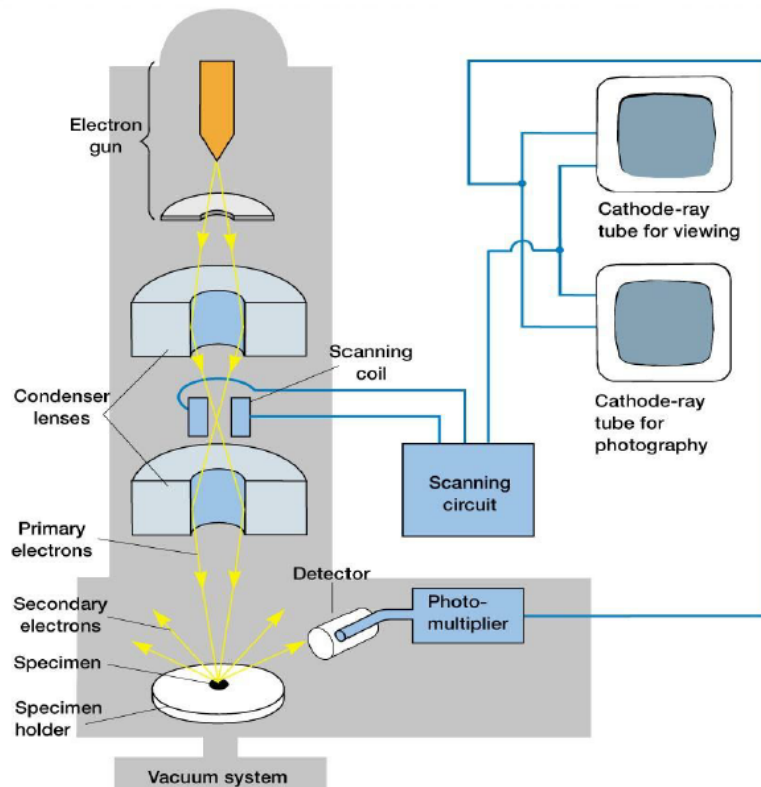


Fig.2.1 Schematic diagram for SEM .

The SEM image formed is the result of the intensity of the secondary electron emission from the sample at each x, y data point during the rastered across the sample, the emitted secondary electrons are collected by a detector, and the output can be used to modulate the brightness of a cathode ray tube(CRT) and produce corresponding image. The resolution and depth of field of the image are determined by the beam current and the final spot size, which are adjusted with one or more condenser lenses and the final, probe forming objective lenses. The schematic diagram for Scanning electron microscope is shown in the Fig.2.1. The lenses are also used to shape the beam to minimize the effects of spherical aberration, chromatic aberration, diffraction, and astigmatism. One of the key advantages of the SEM with respect to other types of microscopy is its large depth of field. This ability makes it possible to image very rough surfaces with millimetres of vertical information within a single image. The depth of field and small beam

size makes it possible to image far below the top layer. This ability also makes it possible to measure very rough surfaces over larger lateral areas as well. For scanning areas that have heights of greater than 5 to 10 μm s of variation, the SEM would be better suited for the analysis.

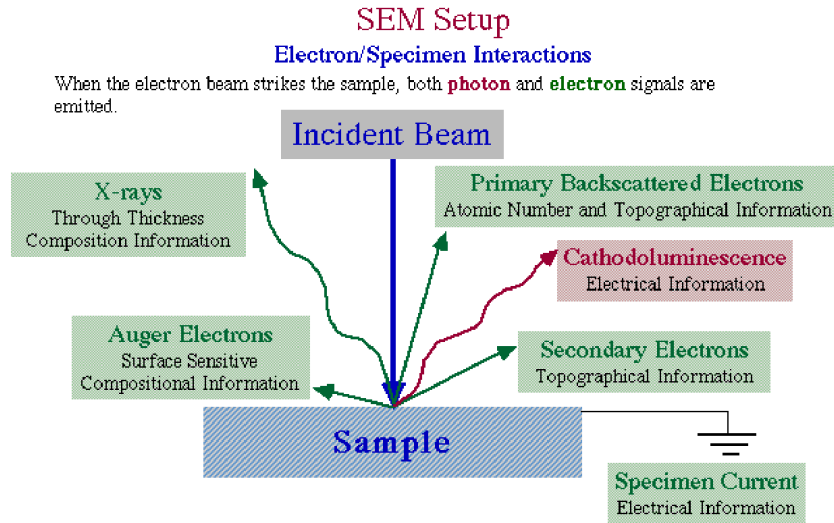


Fig 2.2. Mechanism involve in SEM.

3 Field Emission Scanning Electron Microscopy

Field emission (FE) is a physical phenomena in which, sufficiently intense electric field is applied normal to the surface of a metal or semiconductor, electrons will be emitted through the surface potential barrier into the vacuum, by the quantum mechanical tunnelling effect. The theory of field emission from metals was first derived by Fowler and Nordheim in 1928, who showed that if the temperature is not too high, most of the emitted electrons originate from a small energy interval around the Fermi level of the material. At the other extreme, high temperatures and low fields, electron emission over the potential barrier, rather than it, predominates, i.e. thermionic emission.

Study of field emission characteristics can be done by

- (1). Close proximity configuration
- (2). Conventional field emission microscope.

The field emission studies of the nanostructures have been carried out in the close proximity (CP) configuration wherein the field emitter arrays in the form of a thin film is mounted in

proximity with an anode screen separated by an insulating spacer (~50 μm to a few mm). Electron tunnelling in this configuration is generally referred to as “thin-film tunnelling”. However, such a configuration poses a serious limitation on the strength of the applied electric field as relatively high field may lead to arc formation. Experimental setup of field emission shown in fig.2.10. In the case of the CP configuration, the applied field is usually calculated as $E = V/d$, where V is the applied voltage and d is the separation. This gives an average electric field and not the field at the apex of an individual emitter tip, due to the complexity posed by the large number of emitters on the cathode substrate.

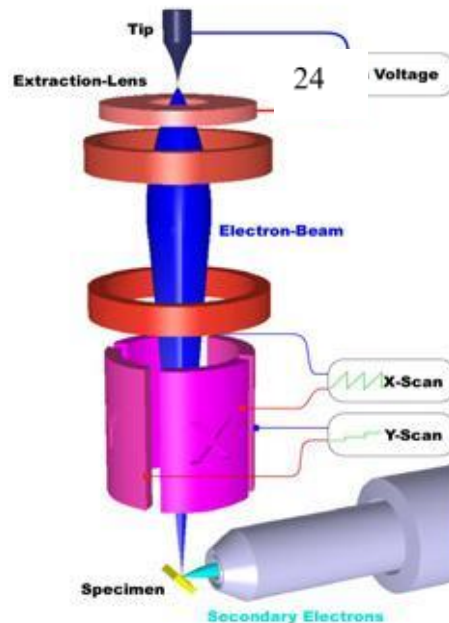


Figure 3. Schematic of a scanning electron microscope with a field emission gun column.

On the other hand, in the conventional FEM configuration, the corresponding field generated at the emitter apex is calculated using $F = \beta_0 V$, and the theoretical field enhancement factor $\beta_0 = 1/kr$, where k is a constant known as the geometrical factor and has the value 5 for a hemispherical emitter, and r is the tip radius. This field is referred to as the local field at the emitter. As a result, comparison of field emitters is pertinent only if the field emission

measurements have been carried out under the same experimental configurations. Fowler-Nordheim predicted the field emitted current density as,

$$J_{FN} = \frac{AE^2}{\phi t^2(y)} \exp\left[\frac{-Bv(y)\phi^{3/2}}{E}\right]$$

Where E is the normal component of electric field at cathode surface, ϕ is the work function where t(y) and v(y) are functions which arises due to the inclusion of image charge effects.

$$y = \left[\frac{(eE/4\pi\epsilon)^{1/2}}{\phi} \right]$$

4.Conclusions:

We have known from this study projet that the characterization techniques XRD (X-ray diffraction) is the most useful and important to know the crystal structure and for the confirmation of the sample. The SEM (scanning electron microscope) is a useful technique to know the morphology of the material.

References:Source: Internet

Acknowledgements:

We thank to Dr.B.Leela, Principal(FAC), Govt.Degree College, Jammikunta for giving the permission to utilize the ICT facilities in the college. We heartfully thank to sri A.Sanjeeva Reddy, Incharge, Department of Physics for his continuous encouragement in doing the projects and career guidance.

