# Nanotechnology techniques: Characterization and Properties of Nanomaterials

# تقنية النانوتكنولوجي: دراسة خواص المواد النانوية

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## الخلاصة

النانوتكنولوجي هي تقنية متقدمة حظيت باهتمام واسع لما لها من القدرة على دراسة الخصائص الفريدة للمواد النانوية وكيفية الاستفادة منها، كما تعد النانوتكنولوجي تقنية جديدة تهتم بهندسة المواد النانوية من خلال تشكيل بنيتها البلورية النانوية ودراسة مكوناتها و خواصها ومعرفة تطبيقاتها، احدثت تقنية النانو نقلة نوعية وتقدمًا كبيرًا في التكنولوجيا، كما كان لها أثرا بارزا في مختلف التقنيات الصناعية، وبالتالي فإن دراسة النانوتكنولوجي في بلادنا أمر ضروري يجب أن يولى اهتماما كبيرا من خلال تنظيم المعرفة المكتسبة من تكنولوجيا النانو لإنشاء نظام القاعدة التكنولوجية التي يمكن أن تسهم في التنمية المستدامة للاقتصاد اليمني، تتميز النانوتكنولوجي بعدة تقنيات لدراسة خصائص المواد النانوية و يركز هذا البحث على اهم هذه التقنيات، حيود الأشعة السينية (**XRD**)، المجهر الالكتروني الماسح (**SEM**)، المجهر الالكتروني النفّاذ (**TEM**) و المجهر الالكتروني عالي النفّاذية (**HRTEM**)

## Abstract

Nanotechnology is an advanced technology received a lot of attention for its ability to make use of the unique properties of nanosized materials. Nanotechnology is new techniques which has been understanding as a technology of design, fabrication and applications of nanostructures and nanomaterials. Nanotechnology is a major advance capable of bringing extraordinary change to various industrial technologies, and thus the establishment of

nanotechnology is vital. And its  includes fundamental understanding of physical properties and phenomena of nanomaterials and nanostructures. Knowledge gained from nanotechnology should be systematized to establish a technological base that can contribute to sustainable development of Yemen's economy. The important techniques of nanotechnology are characterized  by   X-ray diffractometer (XRD). scanning   electron   microscopy (SEM), transmission electron microscopy (TEM) and high resolution TEM. So, this paper presents the  basic theory for X-ray  diffraction and electron microscopy, focusing on the three basic types of  XRD, SEM and TEM.

**Keywords**: Nanotechnology; XRD; SEM; TEM.

# 1. Introduction

Nanotechnology is an advanced technology that has received a lot of attention for its ability to make use of the unique properties of nanosized materials.  Nanoscience and nanotechnology include the areas of synthesis, characterization, exploration, and application of nanomaterials and nanosize materials have been widely studied (1, 4). The properties and behaviors observed and measured are typically group characteristics. A better fundamental  understanding  and various potential  applications increasingly demand the ability and instrumentation to observe, measure and  manipulate  the  individual nanomaterials  and  nanostructures. In general, nanotechnology can be understood as a technology of design, fabrication   and applications  of nanostructures and nanomaterials. also includes fundamental understanding of physical properties and phenomena of nanomaterials and nanostructures.

Nanotechnology  is  an  extension  of  the  discoveries  and applications  of  quantum  mechanics,  its  idea  of  carrying  on manipulations at smaller and smaller scales has been around for quite some time the birth of nanotechnology and widely believed as having

substantial potential to bring benefits to improve research and application (5-8).

The term manipulation lesser smaller scale evolved at the emergence of nanotechnology which takes us back to Richard Feynman presentation on December 1959 at the meeting of the American Physical Society. What he proposed let to have application that permits data storage reduced to the scale of a single atom. As the result, more attentions have been paid to the nanoscience and nanotechnology (3). Nowadays, nanotechnology is a relatively "new" term that is widely discussed and draws the attention of scientists and researchers all over the world (4).

Characterization and manipulation of individual nanostructures require not only extreme sensitivity and accuracy, but also atomic-level resolution. It therefore leads to various microscopy that will play a central role in characterization and measurements of nanostructured materials and nanostructures (9).

Characterization of nanomaterials and nanostructures has been largely based on the surface analysis techniques and conventional characterization methods developed for bulk materials (9).

In the present study, We have studied the characterization techniques of nanotechnology and nanomaterials. Currently, there are a number of sensor technologies and instruments with nanometer scale, or better, sensitivity for measuring and characterizing nanotechnology and nanomaterials, and making all sufficiently precise measurements are first discussed. These include: X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission microscopy (TEM) (10-13).

# 2. Characterization [Structural analysis: SEM, TEM, XRD]

## 2.1 Scanning electron microscopy (SEM)

SEM is one of the most widely used techniques used in characterization of nanomaterial's and nanostructures (9). Moreover, SEM is, next to the optical microscope, one of the most important and versatile tools available for investigations not only in forensic science but many other disciplines in the biological and physical sciences. The first Scanning Electron Microscope (SEM) debuted in 1942 with the first commercial instruments around 1965. Its late development was due to the electronics involved in "scanning" the beam of electrons across the sample (Figure 1) (14).

Electron Microscopes are scientific instruments that use a beam of highly energetic electrons to examine objects on a very fine scale. This examination can yield information about the topography (surface features of an object), morphology (shape and size of the particles making up the object), composition (the elements and compounds that the object is composed of and the relative amounts of them) and crystallographic information (how the atoms are arranged.

The main benefit of SEM is the imaging of solid surfaces and morphology with very high spatial resolution and high depth of focus. With an optical microscope, a spatial resolution down to 0.2 μm and a depth of focus of 1 μm (with magnification 100) is possible. Image generation and magnification taken by SEM is carried out electronically, not optically. Therefore, subsequent image capture and processing systems can come into operation for the analysis of the investigated structures. As the electrons strike and penetrate the surface, a number of interactions occur that result in the emission of electrons and photons from the sample, and SEM images are produced by collecting the emitted electrons on a detector and transferred to cathode ray tube (CRT) Or computer frame store.

### 2.1.1 Elastic and Inelastic Scattering

When a sample is bombarded with electrons, the strongest region of the electron energy spectrum is due to secondary electrons. The secondary electron yield depends on many factors, and is generally higher for high atomic number targets, and at higher angles of incidence. Secondary electrons are produced when an incident electron excites an electron in the sample and loses most of its energy in the process. The excited electron moves towards the surface of the sample undergoing elastic and inelastic collisions until it reaches the surface, where it can escape if it still has sufficient energy.

### 2.1.2 Instrumentation: Structure of SEM [Electron gun]

The first and basic part of the microscopes is the source of electrons. A field emission gun consists of a sharply pointed tungsten tip held at several kilovolts negative potential relative to a nearby electrode, so that there is a very high potential gradient at the surface of the tungsten tip. The result of this is that the  potential energy of an electron as a function of distance from the metal surface has a sharp peak (from the work function), then drops off quickly (due to electron  charge  traveling  through  an  electric field). Because  electrons  are quantum  particles  and  have  a robability distribution to their  location,  a  certain number  of electrons  that  are  nominally  at  the  metal surface  will  find themselves  at  some  distance  from  the  surface,  such  that  they can  reduce  their  energy  by  moving  further  away  from  the surface. This transport-via-delocalization is called 'tunneling', and is the basis for the field emission effect. FEGs produce much higher source brightness than in conventional guns (electron current > 1000 times), better monochromaticity, but requires a very good vacuum (~10-7Pa).

### 2.1.3 Electron-specimen interactions [Electromagnetic Lens (Figure 2)]

When an electron beam interacts with the atoms in a sample, individual incident electrons undergo two types of scattering - elastic and inelastic. In the former, only the trajectory changes and the kinetic energy and velocity remain constant (14).

### 2.1.4 Resolution of optical microscopy

The theoretical limit to an instrument's resolving power is determined by the wavelengths of the electron beam used and the numerical aperture of the system. The resolving power, R, of an instrument is defined as:

$$R = \frac{\lambda}{2NA}$$

where λ is the wavelength of electrons used and NA is the numerical aperture, which is engraved on each objective and condenser lens system, and a measure of the electron gathering ability of the objective, or the electron providing ability of the condenser. For example figure 3 showed that the Rayleigh Limit

$$R = \frac{0.61\lambda}{n_0 \sin \alpha} = \frac{0.61\lambda}{N_A} \qquad \frac{0.61}{\sin \alpha} \cong 1 \quad \text{and} \quad \lambda_{min} \cong 400 \sim 800\ nm$$

R = 400 ≈ 800 nm

λ is Wavelength of light, n0: index of refraction and α: convergence angle. All matter (any object) has a wave-like nature

$$\lambda = \frac{h}{p} \qquad p = mv$$

Where λ is wavelength of light, h is index of refraction and P is convergence angle

Resolution of electron microscope

$$R = \frac{\lambda}{\beta} \qquad \lambda = \frac{h}{p} = \frac{h}{mv} \leftarrow E_{kinetic} = eV = \frac{1}{2}mv^2$$

$$= \frac{h}{\sqrt{2meV}} \cong \sqrt{\frac{150}{V}} \, [\text{Å}]$$

If $V = 150$ V, then $\lambda = 0.1$ nm

Resolution is limited by the lens defects

If $\lambda = 2$–$10$ Å, then $R = 1$–$3$ Å (atomic resolution limit)

### 2.1.5 Scattering

Elastically scattered e- are the major source of contrasts. There are two general theories of diffraction as shown in figure 4:

- Kinematic (scattering from isolated atoms, i.e. x-ray)
- Dynamic (electron diffraction involving wave mechanics)

Common Base (simplified): Bragg's Law

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

Production of secondary electrons is very topography related. Due to their low energy (5eV) only secondaries that are very near the surface (<10 nm) can exit the sample and be examined. Any changes in topography in the sample that are larger than this sampling depth will change the yield of secondaries due to collection efficiencies. Collection of these electrons is aided by using a "collector" in conjunction with the secondary electron detector. presents two secondary electron images from SEM.

## 2.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a key tool for imaging the internal microstructure of ultra-thin specimens. The basic working principle of TEM instrumentation is sketched in Figure 5 (15). In TEM, electrons are accelerated to 100 KeV or higher (up to 1 MeV), projected onto a thin specimen (less than

200nm) by means of the condenser lens system, and penetrate the sample thickness either undeflected or deflected (16).

The greatest advantages that TEM offers are the high magnification ranging from 50 to l06 and its ability to provide both image and diffraction information from a single sample. The scattering processes experienced by electrons during their passage through the specimen determine the kind of information obtained. Elastic scattering involves no energy loss and gives rise to diffraction patterns. Inelastic interactions between primary electrons and sample electrons at heterogeneities such as grain boundaries, dislocations, second-phase particles, defects, density variations, etc., cause complex absorption and scattering effects, leading to a spatial variation in the intensity of the transmitted electrons. In TEM one can switch between imaging the sample and viewing its diffraction pattern by changing the strength of the intermediate lens. The high magnification or resolution of all TEM is a result of the small effective electron wavelengths, which is given by the de Broglie relationship:

$$\lambda = \frac{h}{\sqrt{2mqV}}$$

Where m and q are the electron mass and charge, h is Planck's constant, and V is the potential difference through which electrons are accelerated.

### 2.2.1. Main difficulties in the exploitation of TEM

Transmission Microscopy provides several types of images, as  shown in figure 6(1, 2 and 3). The diffraction patterns show dots, regions or circles originating from the sample area  illuminated  by the  electron  beam  that  depend  on  the  material's  structure. Monocrystals  show  distinguished  dots  in  diffraction  patterns, polycrystalline materials common centred circles and amorphous materials  diffused  circles. Distortions and defects are visible in

bright and dark field images, but expertise is needed in order to interpret whether they are defects or artifacts. Electron or ion beam damages must be considered in TEM analysis, because of the sensibility of the sample and its really low thickness.

The higher the operating voltage of a TEM instrument the greater its lateral spatial resolution. The theoretical instrumental point-to-point resolution is proportional to λ3/4. High-voltage TEM instruments have the additional advantage of greater electron penetration, because high-energy electrons interact less strongly with matter than lower energy electrons. So it is possible to work with thicker samples on a high voltage TEM. One shortcoming of TEM is its limited depth resolution. Electron scattering information in a TEM image originates from a three dimensional sample, but is projected onto a two-dimensional detector. Therefore, structure information along the electron beam direction is superimposed at the image plane.

Selected-area electron diffraction (SAED) (figure 7) offers a unique capability to determine the crystal structure of individual nanomaterials, such as nano-crystals and nanorods, and the crystal structures of different parts of a sample. In SAED, the condenser lens is defocused to produce parallel illumination at the specimen and a selected-area aperture is used to limit the diffracting volume. SAED patterns are often used to determine the Bravais lattices and lattice parameters of crystalline materials by the same procedure used in XRD. Although TEM has no inherent ability to distinguish atomic species, electron scattering is exceedingly sensitive to the target element and various spectroscopy are developed for the chemical composition analysis. Examples include Energy-dispersive X-ray Spectroscopy (EDS) and Electron Energy Loss Spectroscopy (EELS). In addition to the capability of structural characterization and chemical analyses, TEM has been also explored for other applications in nanotechnology. Examples include the determination

of melting points of nano-crystals, in which, an electron beam is used to heat up the nano-crystals and the melting points are determined by the disappearance of electron diffraction. Another example is the measurement of mechanical and electrical properties of individual nanowires and nanotubes.

## 2.3. X-ray Analysis

### 2.3.1 X-Ray Diffraction (XRD)

XRD is a very important experimental technique that has long been used to address all issues related to the crystal structure of solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, preferred orientation of polycrystals, defects, stresses, etc (17-19) To understand diffraction we are in need of two important concepts.

- Rutherford cross-section (see previous slide)
- Atomic scattering factor (fn) → structure factor (F)

$$F = \sqrt{I} = \sum_{n=1}^{N} f_n e^{2\pi i (hu + kv + lw)}$$

Where N is the number of atoms in a unit cell and U,V,W are coordinates of the atom in a unit cell. In XRD, a collimated beam of X-rays, with a wavelength typically ranging from 0.1 to 10 Å, is incident on a specimen and is diffracted by the crystalline phases (Figure 8) in the specimen

According to Bragg's law (20, 21). Bragg's law can be estimated from the peak width with the Scherrer's formula

$\text{Sin } \phi = \frac{XY}{a}$

$XY = a \text{ Sin } \phi$
For 1 and 2 to be in phase and give constructive interference
$XY = 2\lambda, 3\lambda, 4\lambda \ldots\ldots n\lambda$
So a $\text{Sin } \phi = n\lambda$

Where N is the order of diffraction. Diffraction peak positions are accurately measured with XRD, which makes it the best method for characterizing homogeneous and inhomogeneous strains. Homogeneous or uniform elastic strain shifts the diffraction peak positions. From the shift in peak positions, one can calculate the change in d-spacing, which is the result of the change of lattice constants under a strain.

Inhomogeneous strains vary from crystallite to crystallite or within a single crystallite and this causes a broadening of the diffraction peaks that increase with sin 0. Peak broadening is also caused by the finite size of crystallites, but here the broadening is independent of sin 0. When both crystallite size and inhomogeneous strain contribute to the peak width, these can be separately determined by careful analysis of peak shapes.

In addition, X-ray diffraction only provides the collective information of the particle sizes and usually requires a sizable amount of powder. It should be noted that since the estimation would work only for very small particles, this technique is very useful in characterizing nanoparticles. Similarly, the film thickness of epitaxial and highly textured thin films can also be estimated with XRD. One of the disadvantages of XRD, compared to electron diffraction, is the low intensity of diffracted X-rays, particularly for low-Z materials. XRD is more sensitive to high-Z materials, and for low-Z materials, neutron or electron diffraction is more suitable. Typical intensities for electron diffraction are ≈ l08 times larger than for XRD. Because of small diffraction intensities, XRD generally requires large specimens and the information acquired is an average over a large amount of material. Figure 9 XRD in bragg-brentano geometry: single crystal. Specimen.

## Crystal structures of  sample A

Figure 10 shows the XRD patterns of the  Quartz (SiO2) sample A  which take from Amran–Yemen and the crystal structures of the powder SiO2 was characterized by X-ray diffraction (XRD). All the diffraction peaks can be indexed to monoclinic SiO2 (JCPDS no. 2-471).

## Conclusion

Bulk methods are used to characterize the collective information of nanomaterials such as XRD and gas sorption isotherms. They do not provide information of individual nanoparticles or mesopores. Since most nanomaterials have uniform chemical composition and structures, bulk characterization methods are extensively used. SEM is only used for surface images and both resolution and crystallographic information are limited (because they're only referred to the surface). Other constraints are firstly that the samples must be conductive, so non-conductive materials are carbon-coated and secondly, that materials  with atomic number smaller than the carbon are not detected with SEM. As time goes on, the ultimate resolution of the SEM levels out near 0.6nm at 5kV. In  Scanning  Transmission Electron Microscopy in which internal microstructure images of thin specimens are obtained, achieved resolution is up to 1.5nm at 30kV. Important Technological Challenges TEM provides accurate measurements and studies in different types of materials, given that observations are in atomic scale in HRTEM. This is due to technology that reduces the errors and corrects more and more the interferences in  formed images. Today's transmission electron microscopes offer resolutions up to 0.1nm at 300kV and probe diameters up to 0.34nm. Thus, future trends include the use of ultrahigh vacuum TEM instruments for surface studies and  computerized  data acquisition for quantitative image analysis.

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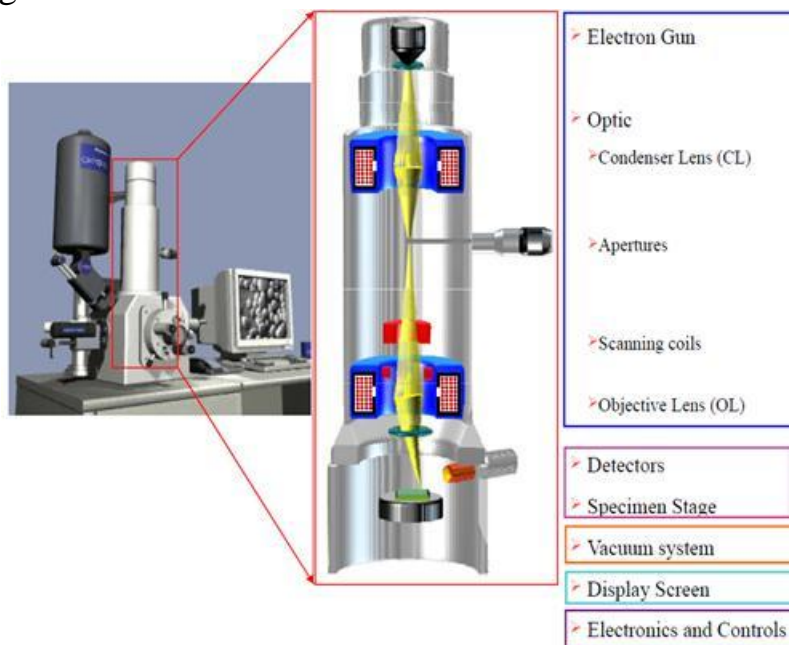
Figure 2.1.1: show the instrumentation: structure of SEM



- Electron Gun
- Optic
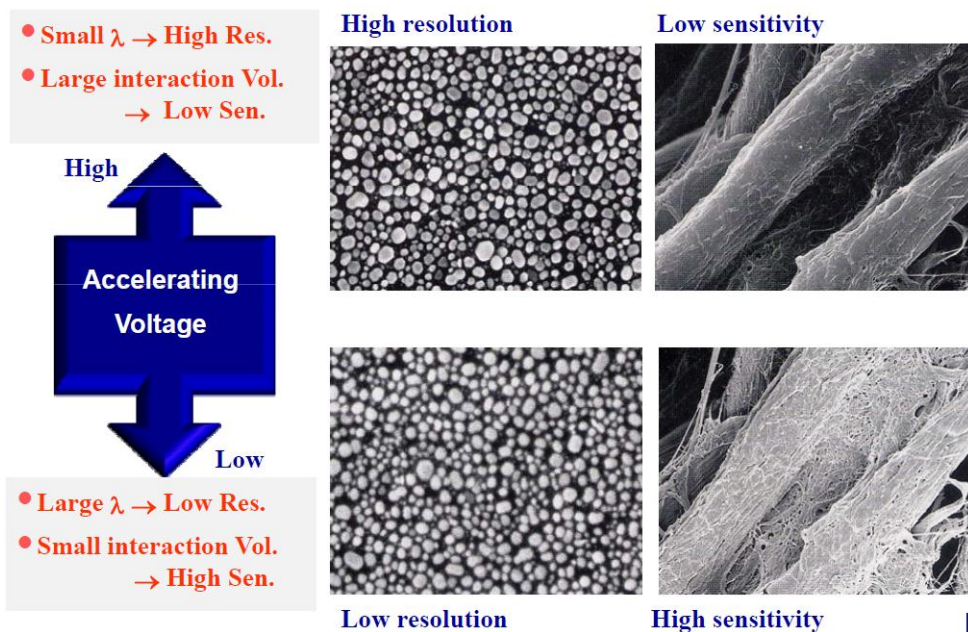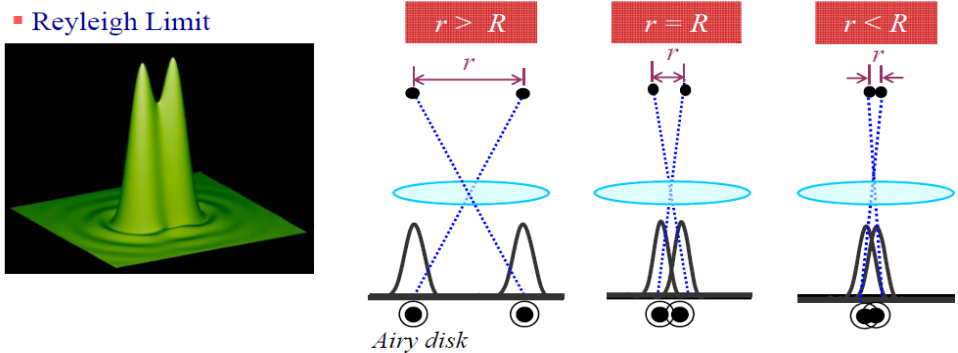  - Condenser Lens (CL)
  - Apertures
  - Scanning coils
  - Objective Lens (OL)
- Detectors
- Specimen Stage
- Vacuum system
- Display Screen
- Electronics and Controls

Figure 2: show the Electromagnetic Lens



- Small λ → High Res.
- Large interaction Vol. → Low Sen.

High

**Accelerating Voltage**

Low

- Large λ → Low Res.
- Small interaction Vol. → High Sen.

High resolution          Low sensitivity

Low resolution          High sensitivity

Figure 3: R: resolution limit → Rayleigh limit



Figure 4: shows SEM samples were prepared with sticking carbon tape glued on sample holder and coated with gold to increase the electrical conduction of the unit, because most SEMs only require the sample to be conductive.



- Field emission gun:
  - Electron beam is produced by electron tunneling.
  - Sharp tip point
  - Several order brighter
  - Ultra high vacuum $10^{-10}$ torr
  - Cold/Thermal/Schottky FE
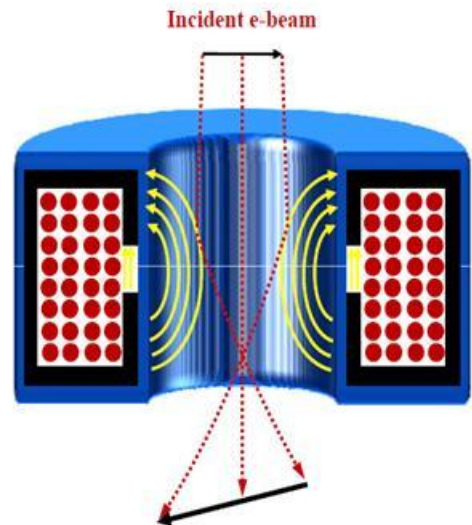
Figure 5: Schematic diagram of the TEM working principle



Cross section of JEM-2010F and assignment of detectors



BF(Dislocation image)



DF(NbC in Steel)



Micrograph is taken by SH OH at the JEM-2010 F, JSI Ljubljana, Slovenia
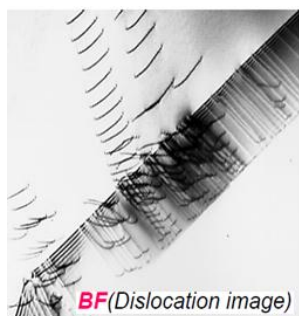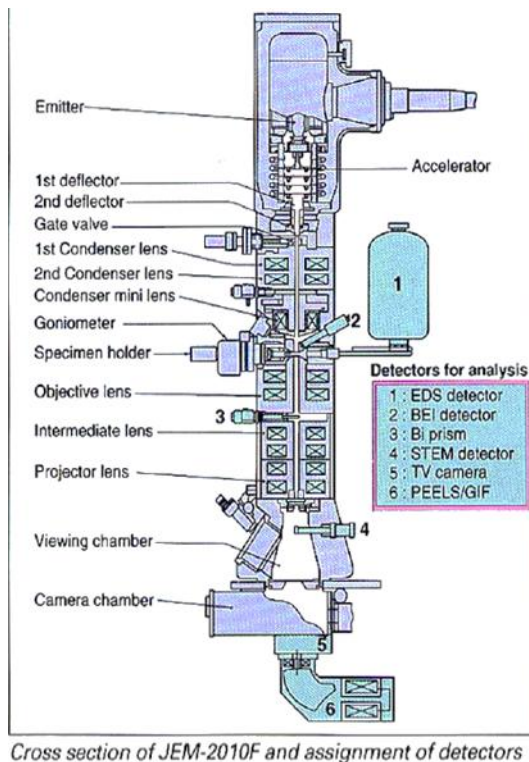
Figure 6.1: shows Bright Field (BF): excludes diffracted electrons. Resolving Power: 1-2nm

Figure 6.2: shows Dark Field (DF): excludes transmitted electrons. Resolving Power: 1-2nm

Figure 6.3 Diffraction pattern of a monocrystalline sample
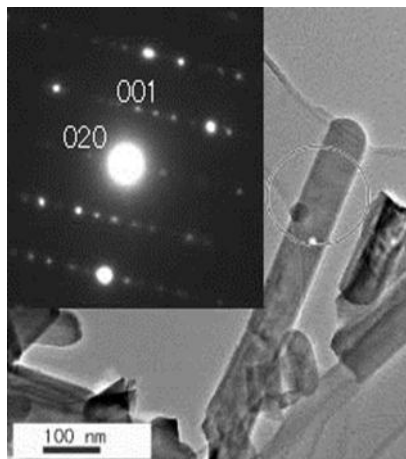
Figure 7: shows the morphological and crystallographic information of small area and the diffraction pattern from a specific region of the specimen using the SAD aperture
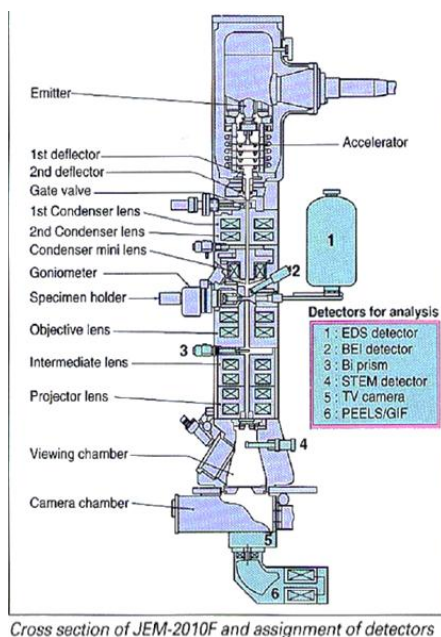


Figure 8: the diffraction an optical grating by the crystalline phases
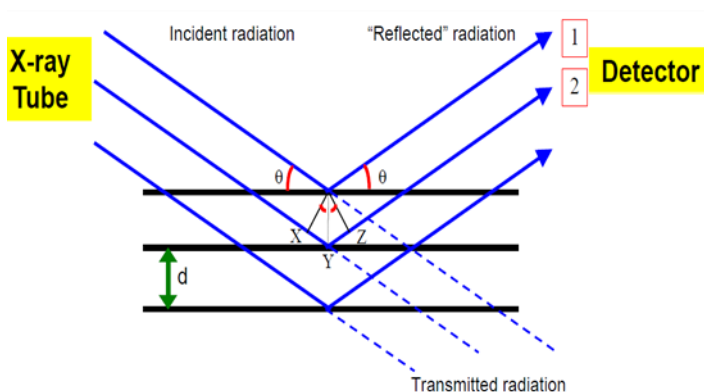Path difference  XY between diffracted beams 1 and 2

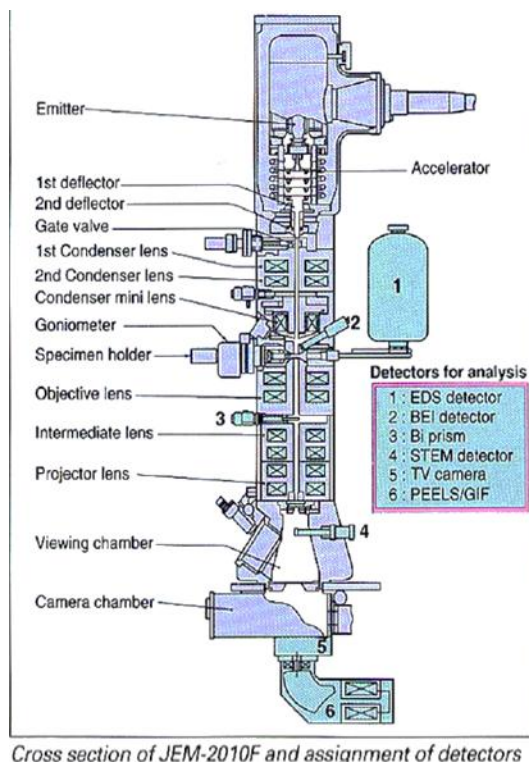Cross section of JEM-2010F and assignment of detectors



Figure 9: shows the powder XRD spectra of a single crystal specimen in a Brentano diffract-meter would produce only one family of peaks in the diffraction pattern.
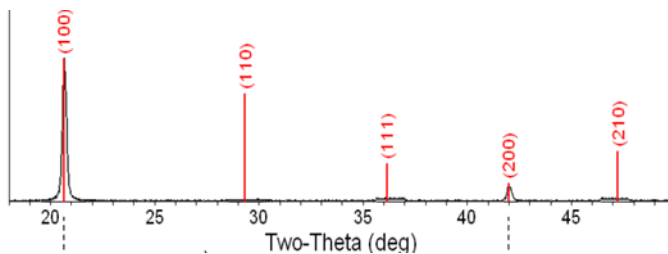
Figure 10: shows the XRD patterns of the  Quartz (SiO2) sample A