NANOPHYSICS (P16 PY E5) UNIT IV

Characterization of Nanomaterials

4.1 Scanning Electron Microscope-SEM

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum in conventional SEM,

Principles

"When the accelerated primary electrons stricks the sample, it produces secondary electrons. These secondary electron are collected by a positive charged electron detector which in turn gives a 3D detector which in turn gives a 3D image of the sample."

The signals used by a scanning electron microscope to produce an image result from interactions of the electron beam with atoms at various depths within the sample. Various types of signals are produced including secondary electrons (SE), reflected or back-scattered electrons(BSE), characteristic X-rays and light (cathodoluminescence) (CL), absorbed current (specimen current) and transmitted electrons. Secondary electron detectors are standard equipment in all SEMs Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

Scanning Electron Microscopy (SEM) - Instrumentation

Construction

It consists of an electron gun to produce high energy electron beam. A magnetic condensing lens is used to condense the electron beam and a scanning coil is arranged in between magnetic condensing lens and the sample. The electron detector (Scintillator) is used to collect the secondary electrons and can be converted into electrical signal. These signals can be fed into CRO through video amplifier as shown in fig.

Working

Stream of electrons are produces by the electron gun and theses primary electrons are accelerated by the grid and anode. These accelerated primary electrons are made to incident on the sample through condensing lenses and scanning coil. These high speed primary electrons on falling over the sample produce low energy secondary electrons. The collection of secondary electrons is very difficult because of their low energy. Therefore, to collect this secondary electron a very high voltage is applied to the collector.

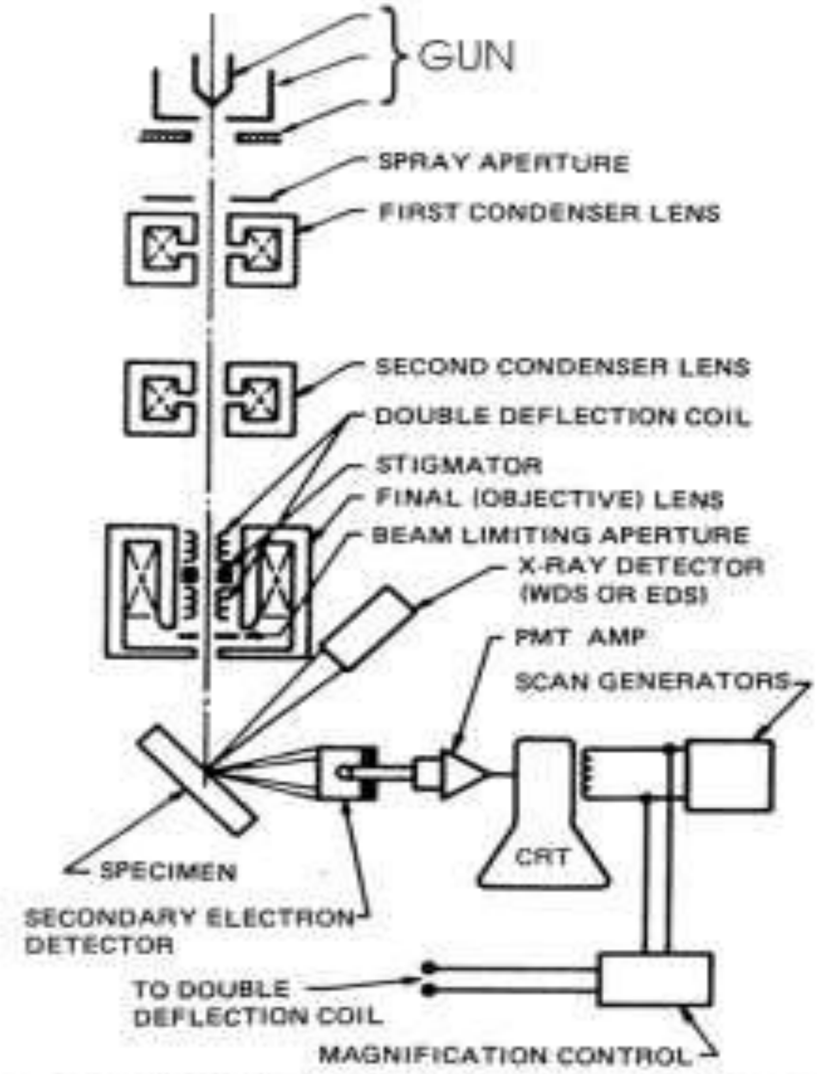


Figure 1.11. Schematic drawing of the electron and x-ray optics of a combined SEM–EPMA.

These collected electrons produce scintillation on photo multiplier tube (detector) and are converted into electrical signals. These signals are amplified by the video amplifier and are fed to the CRO. By similar procedure the electron beam scan the sample from left to right and again from left to right etc., similar to we read a book and the whole picture of the sample is obtained in the CRO screen.

Advantages

1. It can be used to examine specimens of large thickness.
2. It has large depth of focus.
3. It can be used to get a 3D image of the object.
4. Since the image can be directly viewed in the screen, structural details can be resolved in a precise manner.
5. The magnification may be upto 3,00,000 times greater than that of the size of the object.

Disadvantage

1. The resolution of the image is limited to about 10-20 nm, hence it is very poor.

Applications

The SEM is routinely used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions:
1) acquiring elemental maps or spot chemical analyses using EDS,
2)discrimination of phases based on mean atomic number (commonly related to relative density) using BSE, and
3)The SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM.

4.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. The specimen is most often an ultrathin section less than 100 nm thick or a suspension on a grid. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen. The image is then magnified and focused onto an imaging device, such as a fluorescent screen, a layer of photographic film, or a sensor such as a charge-coupled device.

Transmission electron microscopes are capable of imaging at a significantly higher resolution than light microscopes, owing to the smaller de Broglie wavelength of electrons. This enables the instrument to capture fine detail—even as small as a single column of atoms.Transmission electron microscopy is a major analytical method in the physical, chemical and biological sciences. TEMs find application in cancer research, virology, and material science as well as pollution, nanotechnology and semiconductor research.

The first TEM was demonstrated by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolution greater than that of light in 1933 and the first commercial TEM in 1939. In 1986, Ruska was awarded the Nobel Prize in physics for the development of transmission electron microscopy

Principle

Electrons are made to pass through the specimen and the image is formed in the fluoresce screen, either by using transmitted beam (Bright field image) on by using diffracted beam (Dark field image).

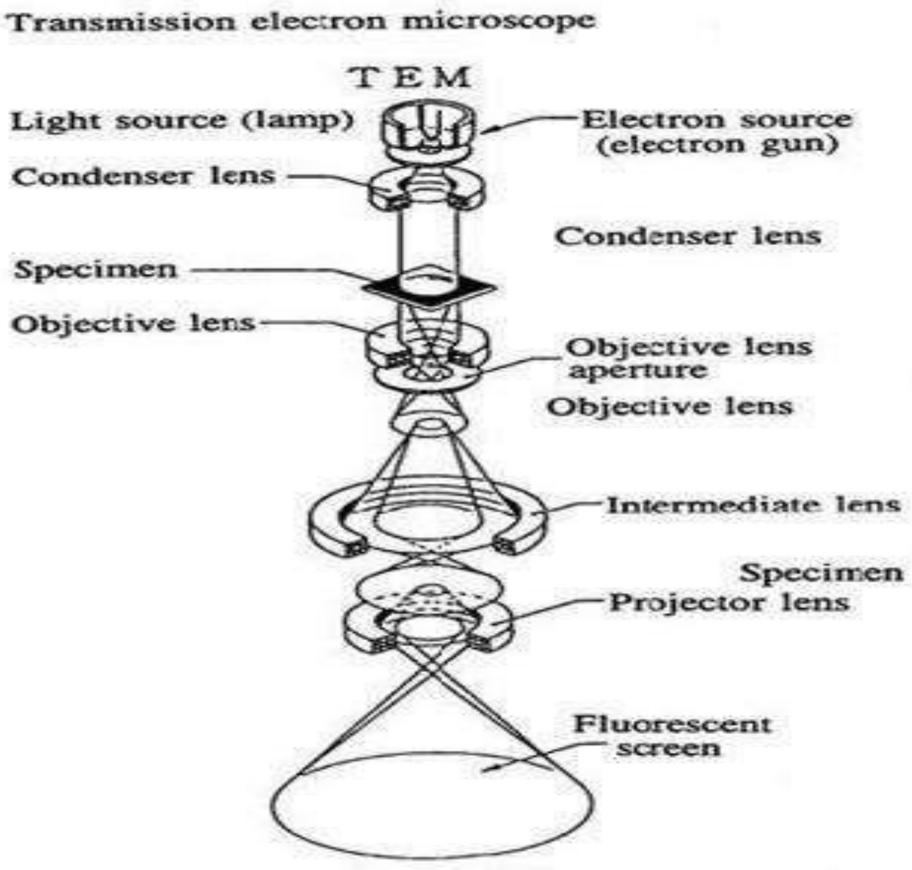
Construction

It consists of an electron gun to produce electrons. Magnetic condensing lens is used to condense the electrons and is also used to adjust the size of the electron that falls onto the specimen. The specimen is places in between the condensing lens and objective lens as show in fig . The magnetic objective lens in used to block the high angle diffracted beams and the aperture is used to eliminate the diffracted beam (if any) and in turn it increases the contrast of the image.The magnetic projector lens is places above the fluorescent screen in order to achieve higher magnification. The image can be recorded by using a florescent (Phosphor) screen or (CCD- charged Coupled Device) also.

Working

Stream of electrons are produced by the electron gun and is made to fall over the specimen using the magnetic condensing lens. Based on the angle of incidence, the beam is partly transmitted and partly diffracted, as shown in fig. Both the transmitted beam and the diffracted beams are recombined at the E-wald sphere (sphere of reflection which encloses all possible reflections from the crystal/specimen, satisfying Bragg‘s law), to form the image as shown in fig . The combined image is called the phase contrast image.

The magnified image is recorded in the fluorescent screen (or) CCD. This high contrast image is called Bright field image. Also, it has to be noted that the bright field image obtained is purely due to the elastic scattering (no energy change) i.e., due to transmitted beam alone.



Advantages

1. It can be used to examine the specimen of size upto 0.2 nm.
2. The magnification is 10,00,000 times greater than the size of the object.
3. It has high resolution
4. The resolving power is 1Å to 2 Å .
5. We can get high contrast image due to both transmitted beams (bright field) and diffracted beam (Dark field).

Disadvantages

1. The specimen should be very thin.
2. It is not suitable for thick samples.
3. There are changes for the structural change, during sample preparation .

4. 3D image can‘t be obtained
5. In case of biological sample, the electron may interact with the sample, which may even damage the sample.

Application

1. The main application of TEM is in Nano science (Nano-tubes, micro machines etc.), used to find the internal structures of nanomaterial.
2. It is used to find the 2D image of very small biological cells. Virus, bacteria etc.
3. It is used in thin film technology, metallurgy, bio-chemistry, micro-biology etc.
4. It is used to study the compositions of paints, papers, fibers, composite materials, alloys etc.

4.3 Scanning Tunneling Microscope

Scanning tunneling microscope (STM), type of microscope whose principle of operation is based on the quantum mechanical phenomenon known as tunneling, in which the wavelike properties of electrons permit them to tunnel beyond the surface of a solid into regions of space that are forbidden to them under the rules of classical physics. The probability of finding such tunneling electrons decreases exponentially as the distance from the surface increases. The STM makes use of this extreme sensitivity to distance.

The sharp tip of a tungsten needle is positioned a few angstroms from the sample surface. A small voltage is applied between the probe tip and the surface, causing electrons to tunnel across the gap. As the probe is scanned over the surface, it registers variations in the tunneling current, and this information can be processed to provide a topographical image of the surface.

The STM appeared in 1981, when Swiss physicists Gerd Binnig and Heinrich Rohrer set out to build a tool for studying the local conductivity of surfaces. Their discovery opened a new era for surface science, and their impressive achievement was recognized with the award of the Nobel Prize for Physics in 1986.

Operating Principle

The STM is an electron microscope with a resolution sufficient to resolve single atoms. The sharp tip in the STM is similar to that in the scanning electron microscope (SEM), In the STM , the tip is positioned close to the sample. The electrons move through the barrier in a way that is similar to the motion of electrons in a metal. In metals, electrons appear to be freely moving particles, but this is illusory. In reality, the electrons move from atom to atom by tunneling through the potential barrier between two atomic sites. In a typical case, with the atoms spaced five angstroms apart, there is a finite probability that the electron will penetrate the barrier and move to the adjacent atom. The electrons are in motion around the nucleus, and they approach the barrier with a frequency of 1017 per second. For each approach to the barrier, the probability of tunneling is 10−4, and the electrons cross the barrier at the rate of 1013 per second. This high rate of transfer means that the motion is essentially continuous and tunneling can be ignored in metals. When the tip is moved close to the sample, the spacing between the tip and the surface is reduced to a value comparable to the spacing between neighbouring atoms in the lattice. In this circumstance, the tunneling electron can move either to the adjacent atoms in the lattice or to the atom on the tip of the probe. The tunneling current to the tip measures the density of electrons at the surface of the sample, and this information is displayed in the image. In semiconductors, such as silicon, the electron density reaches a maximum near the atomic sites. The density maxima appear as bright spots in the image, and these define the spatial distribution of atoms. In metals, on the other hand, the electronic charge is uniformly distributed over the entire surface. The tunneling current image should show a uniform background, but this is not the case. The interaction between tip and sample perturbs the electron density to the extent that the tunneling current is slightly increased when the tip is positioned directly above a surface atom. The periodic array of atoms is clearly visible in the images of materials such as gold, platinum, silver, nickel, and copper.

Procedure

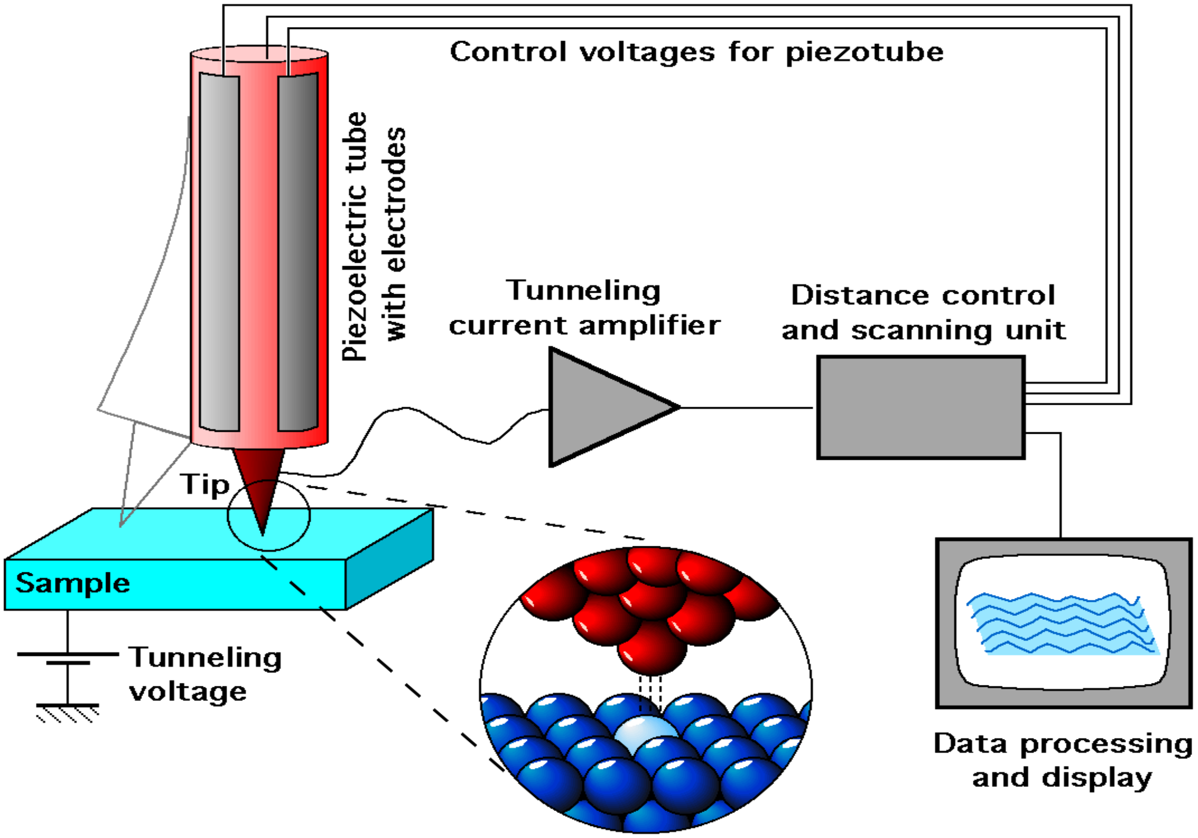
First, a voltage bias is applied and the tip is brought close to the sample by coarse sample-to-tip control, which is turned off when the tip and sample are sufficiently close. At close range, fine control of the tip in all three dimensions when near the sample is typically piezoelectric, maintaining tip-sample separation W typically in the 4-7 Å (0.4- 0.7 nm) range, which is the equilibrium position between attractive (3<W<10Å) and repulsive (W<3Å) interactions. In this situation, the voltage bias will cause electrons to tunnel between the tip and sample, creating a current that can be measured. Once tunneling is established, the tip's bias and position with respect to the sample can be varied (with the details of this variation depending on the experiment) and data are obtained from the resulting changes in current.

If the tip is moved across the sample in the x-y plane, the changes in surface height and density of states causes changes in current. These changes are mapped in images. This change in current with respect to position can be measured itself, or the height, z, of the tip corresponding to a constant current can be measured. These two modes are called constant height mode and constant current mode, respectively.

In constant current mode, feedback electronics adjust the height by a voltage to the piezoelectric height control mechanism. This leads to a height variation and thus the image comes from the tip topography across the sample and gives a constant charge density surface.In constant height mode, the voltage and height are both held constant while the current changes to keep the voltage from changing; this leads to an image made of current changes over the surface, which can be related to charge density.All images produced by STM are grayscale, with color optionally added in post-processing in order to visually emphasize important features.

Instrumentation

The components of an STM include scanning tip, piezoelectric controlled height and x,y scanner, coarse sample-to tip control, vibration isolation system, and computer. The resolution of an image is limited by the radius of curvature of the scanning tip of the STM. The tip is often made of tungsten or platinum-iridium, though gold is also used. Tungsten tips are usually made by electrochemical etching, and platinum-iridium tips by mechanical shearing.



Schematic view of an STM

Advantages

STM is helpful because it can give researchers a three dimensional profile of a surface, which allows researchers to examine a multitude of characteristics, including roughness, surface defects and determining things about the molecules such as size and conformation.
Other advantages of the scanning tunneling microscope include:
1. It has a high resolution in atomic level, which is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution.
2. 3D mapping image can be easily obtained.
3. It is capable of capturing much more details than lesser microscopes.
4. STM is also versatile. They can be used in ultra high vacuum, air, water and other liquids and gasses.
6. They will operate in temperatures as low as zero Kelvin up to a few hundred degrees Celsius.

Disadvantages

The four major downsides to using STMs are:
1. STM can be difficult to use effectively. There is a very specific technique that requires a lot of skill and precision.
2. STM require very stable and clean surfaces, excellent vibration control and sharp tips.
3. STM only can be used to scan not easily oxidized and well conductive samples.
4. STM use highly specialized equipment that is fragile and expensive.

Applications

Several surfaces have been studied with the STM. The arrangement of individual atoms on the metal surfaces of gold, platinum, nickel, and copper have all been accurately documented.

The absorption and diffusion of different species such as oxygen and the epitaxial growth of gold on gold, silver on gold, and nickel on gold also have been examined in detail.

The surfaces of silicon have been studied more extensively than those of any other material. The surfaces are prepared by being heated in vacuum to temperatures so high that the atoms there rearrange their positions in a process called surface reconstruction. The reconstruction of the silicon surface designated (111) has been studied.

The STM can operate in ambient atmosphere as well as in high vacuum. Indeed, it has been operated in air, in water, in insulating fluids, and in the ionic solutions used in electrochemistry.

The STM can be cooled to temperatures less than 4 K (−269 °C, or −452 °F)—the temperature of liquid helium. It can be heated above 973 K (700 °C, or 1,300 °F). The low temperature is used to investigate the properties of superconducting materials, while the high temperature is employed to study the rapid diffusion of atoms across the surface of metals and their corrosion.

4.4 Scanning probe microscope (SPM)

Scanning probe microscope (SPM) is a branch of microscopy that forms images of surfaces using a physical probe that scans the specimen. SPM was founded in 1981, with the invention of the scanning tunneling microscope, an instrument for imaging surfaces at the atomic level. The first successful scanning tunneling microscope experiment was done by Binnig and Rohrer. The key to their success was using a feedback loop to regulate gap distance between the sample and the probe.

Many scanning probe microscopes can image several interactions simultaneously. The manner of using these interactions to obtain an image is generally called a mode.

Among various techniques AFM and STM are the most commonly used for roughness measurements

Image formation

To form images, scanning probe microscopes raster scan the tip over the surface. At discrete points in the raster scan a value is recorded. These recorded values are displayed as a heat map to produce the final STM images, usually using a black and white or an orange color scale.

i). Constant interaction mode

In constant interaction mode (often referred to as "in feedback"), a feedback loop is used to physically move the probe closer to or further from the surface (in the *z* axis) under study to maintain a constant interaction. This interaction depends on the type of SPM, for scanning tunneling microscopy the interaction is the tunnel current, for contact mode AFM or MFM it is the cantilever deflection, etc. The type of feedback loop used is usually a PI-loop, which is a PID loop where the differential gain has been set to zero (as it amplifies noise). The *z* position of the tip (scanning plane is the *xy*-plane) is recorded periodically and displayed as a heat map. This is normally referred to as a topography image.

ii). Constant height mode

In constant height mode the probe is not moved in the *z*-axis during the raster scan. Instead the value of the interaction under study is recorded (i.e. the tunnel current for STM, or the cantilever oscillation amplitude for amplitude modulated non-contact AFM). This recorded information is displayed as a heat map, and is usually referred to as a constant height image.

Constant height imaging is much more difficult than constant interaction imaging as the probe is much more likely to crash into the sample surface. Usually before performing constant height imaging one must image in constant interaction mode to check the surface has no large contaminants in the imaging region, to measure and correct for the sample tilt, and (especially for slow scans) to measure and correct for thermal drift of the sample.

Probe tips

The nature of an SPM probe depends entirely on the type of SPM being used. The combination of tip shape and topography of the sample make up an SPM image. Most importantly the probe must have a very sharp apex. The apex of the probe defines the resolution of the microscope, the sharper the probe the better the resolution. For atomic resolution imaging the probe must be terminated by a single atom.

For many cantilevers based SPMs (e.g. AFM and MFM), the entire cantilever and integrated probe are fabricated by acid [etching], usually from silicon nitride.

Conducting probes, needed for STM and SCM among others, are usually constructed from platinum/iridium wire for ambient operations, or tungsten for UHV operation. Other materials such as gold are sometimes used either for sample specific reasons or if the SPM is to be combined with other experiments such as TERS.

Advantages

1. The resolution of the microscopes is not limited by diffraction, only by the size of the probe-sample interaction volume (i.e., point spread function), which can be as small as a few picometres. Hence the ability to measure small local differences in object height .The interaction can be used to modify the sample to create small structures (Scanning probe lithography).
2. Unlike electron microscope methods, specimens do not require a partial vacuum but can be observed in air at standard temperature and pressure or while submerged in a liquid reaction vessel.