Assignment-5

Experimental methods in Catalysis Assignment

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Scanning Electron Microscope and Transmission electron microscopy

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Scanning Electron Microscope

introduction

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 surface topography and composition of the sample. The electron beam is scanned in a raster scan pattern, and the position of the beam is combined with the intensity of the detected signal to produce an image. In the most common SEM mode, secondary electrons emitted by atoms excited by the electron beam are detected using a secondary electron detector

(Everhart-Thornley detector). The number of secondary electrons that can be detected, and thus the signal intensity, depends, among other things, on specimen topography. SEM can achieve resolution better than 1 nanometer.

The Scanning Electron Microscope (SEM) is used for observation of specimen surfaces. When the specimen is irradiated with a fine electron beam (called an electron probe), secondary electrons are emitted from the specimen surface. Topography of the surface can be observed by two-dimensional scanning of the electron probe over the surface and acquisition of an image from the detected secondary electrons.

History

The basic principles of the scanning electron microscope (SEM) were established in the 1930's and early 1940's by Knoll, Although Max Knoll produced a photo with a 50 mm object-field-width showing channeling contrast by the use of an electron beam scanner and then it was Manfred von Ardenne who in 1937 invented a microscope with high resolution by scanning a very small raster with a demagnified and finely focused electron beam.

Ardenne applied scanning of the electron beam in an attempt to surpass the resolution of the transmission electron microscope (TEM), as well as to mitigate substantial problems with chromatic aberration inherent to real imaging in the TEM. He further discussed the various detection modes, possibilities and theory of SEM, together with the construction of the first high resolution SEM. Further work was reported by Zworykin's group followed by the Cambridge groups in the 1950s and early 1960s headed by Charles Oatley, all of which finally led to the marketing of the first commercial instrument by Cambridge Scientific Instrument Company as the "Stereoscan" in 1965, which was delivered to DuPont.

The SEM was revived by Charles Oatley in a series of PhD projects in the Electrical Engineering Department of Cambridge University in England.

The first industrial application followed from the early work of McMullan and Smith in Cambridge and was at the Pulp and Paper Institute in Canada. This was soon followed by the application of the SEM to integrated circuits at Westinghouse in America and by the availability of commercial SEMs in England and Japan.

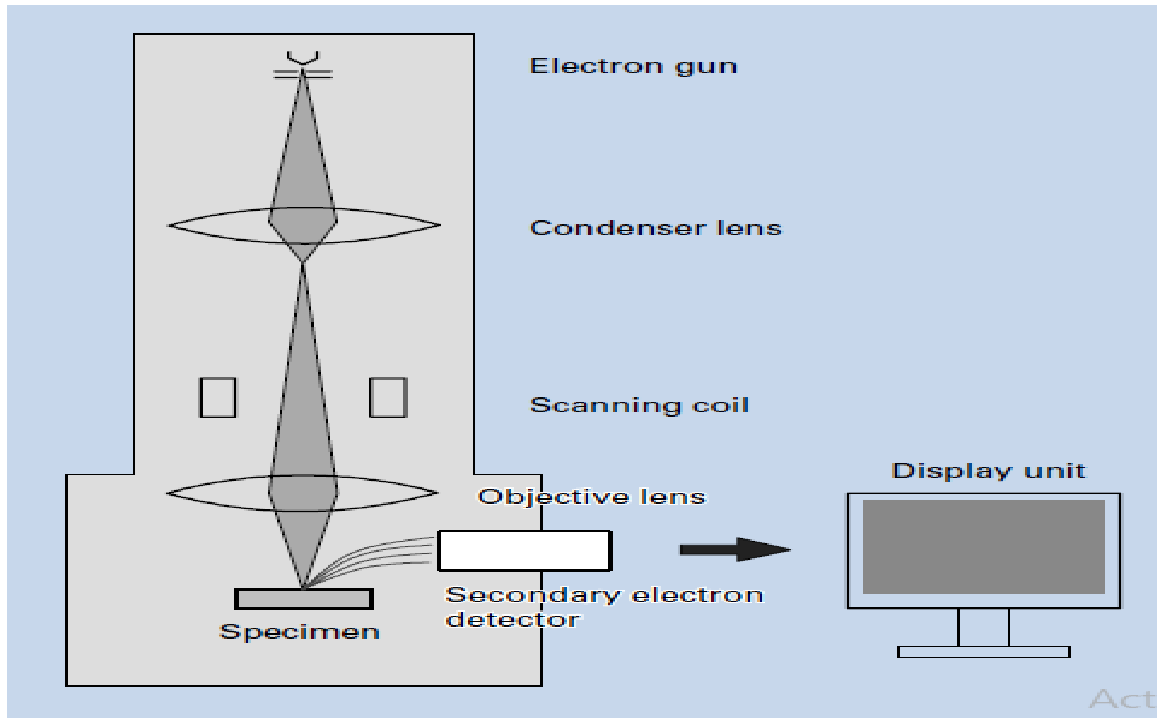
At the present time, the SEM and other microscopic and microanalytical techniques are in a worldwide state of development and are being applied in an increasing number of application areas.

Principles

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), absorbed current (specimen current) and transmitted electrons. Secondary electron detectors are standard equipment in all SEMs, but it is rare for a single machine to have detectors for all other possible signals.

Construction of SEM

The SEM requires an electron optical system to produce an electron probe, a specimen stage to place the specimen, a secondary-electron detector to collect secondary electrons, an image display unit, and an operation system to perform various operations . The electron optical system consists of an electron gun, a condenser lens and an objective lens to produce an electron probe, a scanning coil to scan the electron probe, and other components. The electron optical system (inside of the microscope column) and a space surrounding the specimen are kept at vacuum.



Basic construction of a SEM.

Electron Gun

The electron gun produces an electron beam. Thermoelectrons are emitted from a filament (cathode) made of a thin tungsten wire (about 0.1 mm) by heating the filament at high temperature These thermoelectrons are gathered as an electron beam, flowing into the metal plate (anode) by applying a positive voltage (1 to 30 kV) to the anode.

Specimen Stage

In general, the specimen is observed at a high magnification in an electron microscope. Thus, a specimen stage, which stably supports the specimen and moves smoothly, is required. The specimen stage for a SEM can perform the following movements: horizontal movement (X, Y), vertical movement (Z), specimen tilting (T), and rotation (R). The X and Y movements are used for the selection of a field of view. While the Z movement provides the change of image resolution and the depth of focus.

Secondary Electron Detector

The secondary electron detector is used for detecting the secondary electrons emitted from the specimen. A scintillator (fluorescent substance) is coated on the tip of the detector and a high voltage of about 10 kV is applied to it. The secondary electrons from the specimen are attracted to this high voltage and then generate light when they hit the scintillator. This light is directed to a photo-multiplier tube (PMT) through a light guide. Then, the light is converted to electrons, and these electrons are amplified as an electric signal. A supplementary electrode, called the collector, is placed before the scintillator.

Image Display and Recording

The output signals from the secondary electron detector are amplified and then transferred to the display unit. Since the scanning on the display unit is synchronized with the electron-probe scan, brightness variation, which depends on the number of the secondary electrons, appears on the monitor screen on the display unit, thus forming a SEM image liquid-crystal display (LCD) has been widely used as a display unit . In general, the scan speed of the electron probe can be changed in several steps, An extremely fast scan speed is used for observation and a slow scan speed is used for acquisition or saving of images.

Vacuum System

The inside of the electron optical system and the specimen chamber must be kept at a high vacuum of 10-3 to 10-4 Pa. Thus, these components are evacuated generally by a diffusion pump. If a user desires an oil-free environment, a turbo molecular pump may be used. When a SEM incorporates an FE gun (explained later), a sputter ion pump is used because the FE gun needs an ultrahigh vacuum. To exchange a specimen, either of two methods is applied. One vents the entire specimen chamber at the time of specimen exchange. The other uses a specimen pre-evacuation chamber (airlock chamber) while keeping a high vacuum in the specimen chamber.

Scanning process and image formation

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapor pressure of all metals, thereby allowing it to be electrically heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded or field emission guns (FEG),

which may be of the cold-cathode type using tungsten single crystal emitters or the thermally assisted Schottky type, that use emitters of zirconium oxide.

The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the *x* and *y* axes so that it scans in a raster fashion over a rectangular area of the sample surface. Mechanisms of emission of secondary electrons, backscattered electrons, and characteristic X-rays from atoms of the sample When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to approximately 5 µm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a computer monitor.

APPLICATIONS OF SEMS

MATERIALS SCIENCE

SEMs are used in materials science for research, quality control and failure analysis.In modern materials science, investigations into nanotubes and nanofibres, high temperature superconductors, mesoporous architectures and alloy strength, all rely heavily on the use of SEMs for research and investigation. In fact, just about any material science industry, from aerospace and chemistry to electronics and energy usage, have only been made possible with the help of SEMs.

NANOWIRES FOR GAS SENSING

Researchers are exploring new ways nanowires can be used as gas sensors by improving existing fabrication methods and developing new ones. Electron

microscopy is vitally important in helping characterise nanowires and understanding their gas sensing behaviour.

SEMICONDUCTOR INSPECTION

Reliable performance of semiconductors requires accurate topographical information. The high resolution three dimensional images produced by SEMs offers a speedy, accurate measurement of the composition of the semiconductor.

In fact, in just about all wafer manufacturing processes, SEMs are one of three essential quality control tools used. In the case of repetitive daily quality control tests, larger monitors (19 inches) have been shown to reduce visual fatigue for inspectors.

MICROCHIP ASSEMBLY

Microchip production is increasingly relying on SEMs to help gain insight into the effectiveness of new production and fabrication methods. With smaller and smaller scales and materials, as well as the potential of complex self assembling polymers, the high resolution, three-dimensional capacity of SEMs is invaluable to microchip design and production.

Transmission Electron Microscope

Introduction

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

Transmission electron microscopy is used to reveal sub-micrometre, internal fine structure in solids. The amount and scale of the information which can be extracted by TEM depends critically on four parameters; the resolving power of the microscope (usually smaller than 0.3 nm); the energy spread of the electron beam (often several eV); the thickness of the specimen (almost always significantly less than 1 μm), and; the composition and stability of the specimen.

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, which is thousands of times smaller than a resolvable object seen in a light microscope. Transmission electron microscopy is a major analytical method in the physical, chemical and biological sciences.

TEMs find application in cancer research, virology, and materials science as well as pollution, nanotechnology and semiconductor research, but also in other fields such as paleontology and palynology.

History

In 1873, Ernst Abbe proposed that the ability to resolve detail in an object was limited approximately by the wavelength of the light used in imaging or a few hundred nanometers for visible light microscopes. Developments in ultraviolet (UV) microscopes, led by Kohler and Rohr, increased resolving power by a factor of two. However this required expensive quartz optics, due to the absorption of UV by glass. It was believed that obtaining an image with sub-micrometer information was not possible due to this wavelength constraint.

Knoll's research group was unaware of this publication until 1932, when they quickly realized that the De Broglie wavelength of electrons was many orders of magnitude smaller than that for light, theoretically allowing for imaging at atomic scales. (Even for electrons with a kinetic energy of just 1 volt the wavelength is already as short as 1.23 nm.) In April 1932, Ruska suggested the construction of a new electron microscope for direct imaging of specimens inserted into the microscope, rather than simple mesh grids or images of apertures. With this device successful diffraction and normal imaging of an aluminium sheet was achieved. However the magnification achievable was lower than with light microscopy. Magnifications higher than those available with a light microscope were achieved in September 1933 with images of cotton fibers quickly acquired before being damaged by the electron beam.

interest in the electron microscope had increased, with other groups, such as that of Paul Anderson and Kenneth Fitzsimmons of Washington State University and that of Albert Prebus and James Hillier at the University of Toronto, who constructed the first TEMs in North America in 1935 and 1938, respectively, continually advancing TEM design.

In 1939, the first commercial electron microscope, pictured, was installed in the Physics department of IG Farben-Werke. Further work on the electron microscope was hampered by the destruction of a new laboratory constructed at Siemens by an air raid.

<u>Components of TEM;</u>

A TEM is composed of several components, which include a vacuum system in which the electrons travel, an electron emission source for generation of the electron stream, a series of electromagnetic lenses, as well as electrostatic plates. The latter two allow the operator to guide and manipulate the beam as required. Also required is a device to allow the insertion into, motion within, and removal of specimens from the beam path. Imaging devices are subsequently used to create an image from the electrons that exit the system.

Vacuum system

To increase the mean free path of the electron gas interaction, a standard TEM is evacuated to low pressures, typically on the order of 10^{-4} Pa. The need for this is twofold: first the allowance for the voltage difference between the cathode and the

ground without generating an arc, and secondly to reduce the collision frequency of electrons with gas atoms to negligible levels—this effect is characterized by the mean free path. TEM components such as specimen holders and film cartridges must be routinely inserted or replaced requiring a system with the ability to re-evacuate on a regular basis. As such, TEMs are equipped with multiple pumping systems and airlocks and are not permanently vacuum sealed.

Specimen stage

TEM specimen stage designs include airlocks to allow for insertion of the specimen holder into the vacuum with minimal loss of vacuum in other areas of the microscope. The specimen holders hold a standard size of sample grid or self-supporting specimen. Standard TEM grid sizes are 3.05 mm diameter, with a thickness and mesh size ranging from a few to 100 µm. The sample is placed onto the meshed area having a diameter of approximately 2.5 mm. Usual grid materials are copper, molybdenum, gold or platinum. This grid is placed into the sample holder, which is paired with the specimen stage. A wide variety of designs of stages and holders exist, depending upon the type of experiment being performed. In addition to 3.05 mm grids, 2.3 mm grids are sometimes, if rarely, used. These grids were particularly used in the mineral sciences where a large degree of tilt can be required and where specimen material may be extremely rare. Electron transparent specimens have a thickness usually less than 100 nm, but this value depends on the accelerating voltage.

Electron gun

The electron gun is formed from several components: the filament, a biasing circuit, a Wehnelt cap, and an extraction anode. By connecting the filament to the negative component power supply, electrons can be "pumped" from the electron gun to the anode plate and the TEM column, thus completing the circuit. The gun is designed to create a beam of electrons exiting from the assembly at some given angle, known as the gun divergence semi-angle, α. By constructing the Wehnelt cylinder such that it has a higher negative charge than the filament itself, electrons that exit the filament in a diverging manner are, under proper operation, forced into a converging pattern the minimum size of which is the gun crossover diameter.

Electron lens

Electron lenses are designed to act in a manner emulating that of an optical lens, by focusing parallel electrons at some constant focal distance. Electron lenses may operate electrostatically or magnetically. The majority of electron lenses for TEM use electromagnetic coils to generate a convex lens. The field produced for the lens must be radially symmetrical, as deviation from the radial symmetry of the magnetic lens causes aberrations such as astigmatism, and worsens spherical and chromatic aberration. Electron lenses are manufactured from iron, iron-cobalt or nickel cobalt alloys.

Apertures

Apertures are annular metallic plates, through which electrons that are further than a fixed distance from the optic axis may be excluded. These consist of a small metallic disc that is sufficiently thick to prevent electrons from passing through the disc, whilst permitting axial electrons. This permission of central electrons in a TEM causes two effects simultaneously: firstly, apertures decrease the beam intensity as electrons are filtered from the beam, which may be desired in the case of beam sensitive samples. Secondly, this filtering removes electrons that are scattered to high angles, which may be due to unwanted processes such as spherical or chromatic aberration, or due to diffraction from interaction within the sample.

Modifications

The capabilities of the TEM can be further extended by additional stages and detectors, sometimes incorporated on the same microscope.

Scanning TEM

A TEM can be modified into a scanning transmission electron microscope (STEM) by the addition of a system that rasters a convergent beam across the sample to form the image, when combined with suitable detectors. Scanning coils are used to deflect the beam, such as by an electrostatic shift of the beam, where the beam is then collected using a current detector such as a Faraday cup, which acts as a direct electron counter. By correlating the electron count to the position of the scanning beam , the transmitted component of the beam may be measured. The non-transmitted components may be obtained either by beam tilting or by the use of annular dark field detectors.

Low-voltage electron microscope

A low-voltage electron microscope (LVEM) is operated at relatively low electron accelerating voltage between 5–25 kV. Some of these can be a combination of SEM, TEM and STEM in a single compact instrument. Low voltage increases image contrast which is especially important for biological specimens.

Cryo-TEM

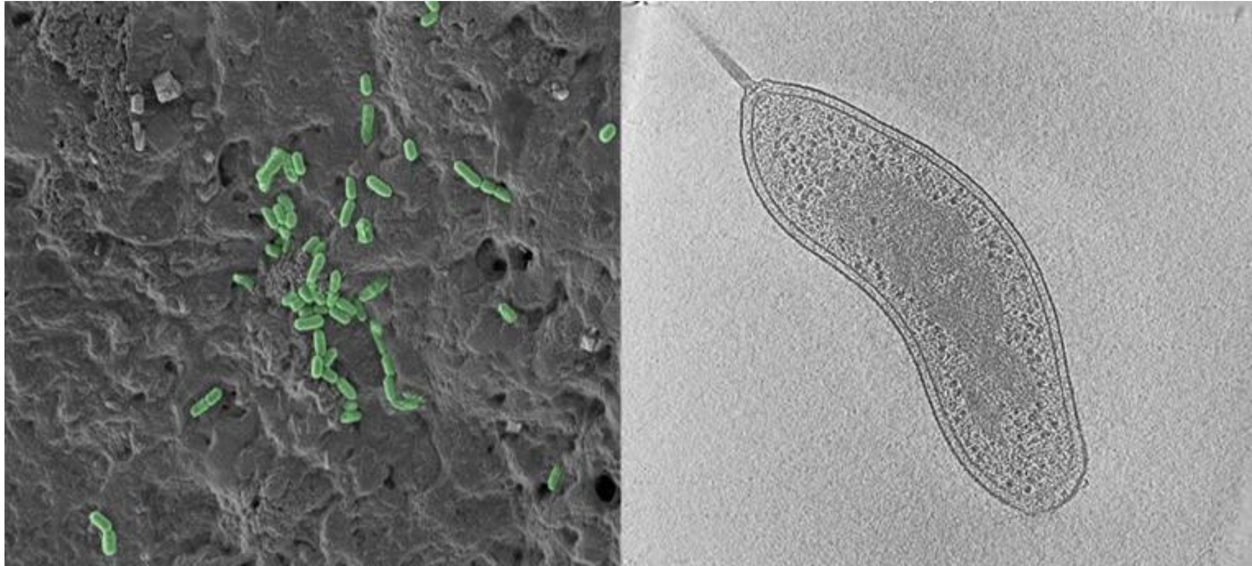
Cryogenic transmission electron microscopy (Cryo-TEM) uses a TEM with a specimen holder capable of maintaining the specimen at liquid nitrogen or liquid helium temperatures.

Transmission (TEM) vs Scanning (SEM) Electron Microscopes

Scanning Electron Microscope (SEM)	Transmission Electron Microscope (TEM)
Used to produce excellent images of the surfaces of cells and small organisms. Excellent for studying surface morphology of the organisms, cells or any suitable material under study	Used to study the ultra structure of the cell and its components. It can see objects as small as a protein molecule or even at nano level. Provides details about internal composition of cells or any suitable material under study
Electron beam scans over the surface of the sample	Electron beam pass through the sample
Based on scattered electrons or produces images by detecting secondary electrons which are emitted from the surface due to excitation by the primary electron beam	Based on transmitted electrons or produces images by detecting primary electrons transmitted from the sample
Comparatively low resolution than TEM; Resolution: 2nm(Average), 0.2nm (Special)	High Resolution; Resolution: 10 nm (Average), 0.5nm (Special)
Depth of field: High	Depth of field: Moderate
Magnifying power: 100,000X	Magnifying power: 5,000,000X
Specimen contrast: by electron adsorption	By electron scattering
Produces three-dimensional black and white images	Produces two-dimensional black and white images
Preparation technique: easy	Skilled, very thin sample is required
Preparation thickness: variable	Very thin
Specimen mounting: Aluminium stubs	Thin films on copper grids
Field of view: Large	Limited

Overall, TEM offers unparalleled detail but can only be used on a limited range of specimens and tends to be more demanding than SEM. It is important to note that advanced techniques such as cryo-EM, a method which looks at typically

biological specimen in a vitrified, amorphous state, have expanded the capabilities of TEM significantly. In particular, healthcare may benefit from the details and mechanisms at the molecular and cellular level that are currently revealed by cryo-EM.



SEM (left) and TEM (right) images of bacteria. Whereas SEM shows numerous bacteria on a surface (green), the TEM image shows the interior structure of a single bacterium.