Concept and history of scanning electron microscope & electron microprobe

Development of quantum theory

John Dalton (1766-1844)
1808 Every element consists of indivisible particles called atoms

James Clerk Maxwell (1831-1879)
1865 Maxwell's field equations –
   The birth of field theory (from Faraday)
   The electromagnetic theory of light
   Light propagates as waves

Johann Balmer (1825-1898)
1885 Discovers numerological relationship between frequency and prominent spectral lines of hydrogen:

\[ \nu_n = c R \left( \frac{1}{n^2} - \frac{1}{2^2} \right) \]

\( n = \) integer
\( \nu = \) frequency
\( c = \) speed of light
\( R = \) Rydberg constant
Wilhelm Conrad Röntgen (1845-1923)  
1895  Discover X-rays in experiments with passing electric current through low-pressure gas  
In German-speaking countries, X-ray are still called “Röntgenstrahlen” (ray of Röntgen) 
First Nobel Prize in 1901 in Physics!

J.J. Thompson (1856-1940)  
1897  Identifies “cathode rays” as negative particles = electrons

Max Plank (1858-1947)  
1901  Introduces the quantum concept - Absorption and emission of radiant energy in discrete packets  
\[ E = h \nu \]  
\[ h = 6.6262 \times 10^{-34} \text{ kg m}^2 / \text{sec} \]  
Nobel Prize in 1918.

Albert Einstein (1879-1955)  
1905  Photoelectric effect and the photon concept. Special relativity too! Nobel Prize in 1921.

Charles G. Barkla (1877-1944) & C.A. Sadler  
1909  Observation of characteristics X-ray produced by electron bombardment of pure element. However at that time, the physics of X-ray was still unclear… Nobel Prize in 1917.

Ernest Rutherford (1871-1937)  
1911  An atom consists of a positively charged nucleus and negatively charged electrons orbiting the nucleus at constant speed. Nobel Prize in 1908.
Niels Bohr (1885-1962)
1913 Quantum model of hydrogen
(early quantum theory)

Predicts the Rydberg constant and the line spectra for gaseous hydrogen. Nobel Prize 1922.

Bohr’s Three Postulates:

1) There are certain orbits in which the electron is stable and does not radiate. The energy of an electron in an orbit can be calculated - that energy is directly proportional to the distance from the nucleus.

Bohr simply forbids electrons from occupying just any orbit around the nucleus such that they can’t lose energy and spiral in...

2) When an electron falls from an outer orbit to an inner orbit, it loses energy expressed as a quantum of electromagnetic radiation.

2) A relationship exists between the mass, velocity and distance from the nucleus of an electron and Planck’s quantum constant...

From these principles, Bohr realized he could calculate the energy corresponding to an orbit:

\[ E_n = -\frac{me^4}{2\hbar^2} \cdot \frac{1}{n^2} \]

\[ \Delta E = \frac{me^4}{2\hbar^2} \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \]

If an electron jumps from orbit \( n = 2 \) to orbit \( n \), the energy change is:
Modern quantum theory:

Louis de Broglie (1892-1987)

1924  Wave theory of matter, ultimately led to the development of wave mechanics

\[ \lambda = \frac{h}{p} = \frac{h}{mv} \sqrt{1 - \frac{v^2}{c^2}} \]

\( \lambda \) Particle wavelength
\( h \) Planck’s constant
\( p \) Particle momentum
\( m \) Rest mass
\( v \) Particle velocity

Modified equation for electron:
Momentum & velocity calculated from acceleration voltage…

\[ \lambda_e = \frac{hc}{Vq_e (2m_e c^2 + Vq_e)} \approx \frac{h}{\sqrt{2Vq_e m_e}} \]

\( \lambda_e \) Electron wavelength
\( h \) Planck’s constant
\( c \) Light speed
\( V \) Acceleration voltage
\( q_e \) Electron charge
\( m_e \) Electron rest mass

Relativistic theory (mass change with velocity)

Newtonian theory (mass constant)

Wolfgang Pauli (1900-1958)

1925  The exclusion principle: No two electrons can be in the same place at the same time.

Electrons in an atom can be described by four quantum numbers (*). No two electrons in an atom can have the same set of quantum numbers ➔ Electron orbitals…

(*) Quantum numbers

- \( n \) principal-shell (1, 2, 3… = K, L, M)
- \( l \) azimuthal-subshell (s, p, d, f…)
- \( m_l \) magnetic, energy shift (= ±)
- \( m_s \) spin, (1/2 or -1/2)

Further refinement of atom model and behavior (quantum physics) by…

- Werner Heisenberg (1901-1976)
- Erwin Schrödinger (1887-1961)
- Max Born (1882-1970)
- Paul Dirac (1902-1984)
- Hans Bethe (1906-2005)

…but not discussed here.
Development of concepts - SEM

Ernst Abbe (1840-1905)
1878  Geometric optics & resolving power of a microscope

What is resolution?
- All lens images are diffraction patterns (circular slit diffraction)
- An image point will be a disk, surrounded by diffraction rings representing diffraction maxima & minima

Rayleigh Criterion: Central maximum produced by one object point must exceed the first diffraction minimum of the other object point...

Diffraction pattern resulting from a uniformly-illuminated circular aperture
⇒ Airy disk (named after George B. Airy, 1801-1892)
Maximum resolution of a microscope (resolving power) is determined by the \textit{wavelength} of the particle used for imaging (e.g. light, electron, x-ray).

Far away from the aperture, the angle \( \Theta \) at which the first minimum occurs is approximately

\[
\sin \Theta = \frac{1.22 \lambda}{d}
\]

\( d \) = lens or aperture diameter
\( \lambda \) = wavelength of particle (e.g. light)

At small angles...

\[
\Theta = \frac{1.22 \lambda}{d}
\]

\textbf{Abbe equation for resolution}

\[
S = \frac{1.22 \lambda}{2n \sin \alpha}
\]

\( S \) = resolution (resolving power)
\( n \) = refractive index (1 for vacuum)
\( \alpha \) = aperture angle

1) \textit{Visible light}

\( \lambda = 560 \) nm

Aperture angle \( \alpha = 0.9 \) nm

\( n = 1 \)

\[
S = \frac{1.22(560)}{2(0.016)} = 20,000 \text{ nm}
\]

2) \textit{Electrons}

\( \lambda = 0.0054 \) nm (*)

Aperture angle \( \alpha = 0.9 \) nm

\( n = 1 \)

\[
S = \frac{1.22(0.0054)}{2(0.016)} = 0.21 \text{ nm}
\]

(*) remember de Broglie and the wave theory of matter...

\textbf{H O W E V E R, true resolution depends on...}

1) \textit{Beam brightness} (shape/size of the original cone of light/electron)
2) \textit{Lens aberrations} (e.g. chromatic aberrations, astigmatism)
3) \textit{Scattering in specimen}
Resolution for electron at variable acceleration voltage

Using **relativistic equations** (Einsteinian equation: mass changes with velocity)
or **classical physics** (Newtonian equation: mass is fixed)

<table>
<thead>
<tr>
<th>Electron V</th>
<th>Mass (kg)</th>
<th>Relativistic Mass</th>
<th>Wavelength (nm)</th>
<th>Abbe resolution (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 keV</td>
<td>9.20e-31</td>
<td>1.0097</td>
<td>0.0173</td>
<td>10.588</td>
</tr>
<tr>
<td>9.11e-31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 keV</td>
<td>9.29e-31</td>
<td>1.0195</td>
<td>0.0122</td>
<td>7.468</td>
</tr>
<tr>
<td>9.11e-31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 keV</td>
<td>9.47e-31</td>
<td>1.0391</td>
<td>0.0086</td>
<td>5.256</td>
</tr>
<tr>
<td>9.11e-31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 keV</td>
<td>10.00e-31</td>
<td>1.0978</td>
<td>0.0054</td>
<td>3.277</td>
</tr>
<tr>
<td>9.11e-31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200 keV</td>
<td>12.67e-31</td>
<td>1.3913</td>
<td>0.0025</td>
<td>1.535</td>
</tr>
<tr>
<td>9.11e-31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400 keV</td>
<td>16.24e-31</td>
<td>1.7827</td>
<td>0.0016</td>
<td>1.006</td>
</tr>
<tr>
<td>9.11e-31</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Assuming a fixed angular aperture of ~0.57°

\[ \sin(\sim0.57°) = 0.01 \]

Mass of electron = 9.1091 x 10^{-31} kg
Speed of light = 2.9979 x 10^8 m/sec
Planck’s Constant = 6.6256 x 10^{-34} m^2 kg/sec

Source: "Accelerating voltage physics calculator"
University of Oklahoma, electron microscopy laboratory

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Richard T. Beatty (1882-1941)
1912-13 electrons produced 2 types of X-ray: (a) Bremsstrahlung and (b) characteristic radiation only when electrons have high enough energy.

Henry Moseley (1887-1915)
1913 Following Bohr’s work, he demonstrates that the wavelengths of emitted X-rays correlates with atomic number

Moseley’s Law:

\[ \sqrt{f} = k_1 (Z - k_2) \]

Or... \[ \lambda = \frac{K}{(Z - k_2)^2} \]

\( f = \text{frequency} \)
\( Z = \text{atomic number} \)
\( \lambda = \text{wavelength} \)
\( k_1, k_2 = \text{constants} \)
\( c = \text{speed of light} \)
\( K = c/(k_1)^2 \)

Max von Laue (1879-1960)
1914 A beam of X-rays passing through a crystal produces a diffraction pattern.
**Karl Manne G. Siegbahn (1886-1978)**

1914 Discovered **M-series of wavelengths** in X-ray emission spectra, and developed methodology and instrumentation for detailed X-ray spectroscopy.

1923 Lays out the Siegbahn notation for X-ray (Kα, Kβ, Lα, Lβ, Lγ…) and modify Bragg’s law (*) to include effect of refraction.

**William Bragg (1864-1942)**

& his son, W. Lawrence Bragg (1890-1971)

1915 Pioneer the analysis of crystal structure using X-ray diffraction. **Bragg’s law.**

*Nobel prize in 1915.

Bragg’s law: 

\[ n\lambda = 2d \sin \theta \]

(*) Modified Bragg’s law:

\[ n\lambda = 2d(1 - k / n^2) \sin \theta \]

\( n \) = diffraction order  
\( \lambda \) = X-ray wavelength  
\( d \) = crystal lattice spacing  
\( \theta \) = diffraction angle  
\( k \) = refraction index **

**SEM and EPMA development**

**Georg K. von Hevesy (1885-1966)**

1923 Development of the **X-ray fluorescence technique**, discovery of Hf (Nobel Prize in 1943)

**Hans Busch (1884-1973)**

1926 Establishes **geometrical electron optics** theoretically

**Hugo Stintzing (1854–1933)**

1927 Develops the cathode-ray scanning microphotometer, and essentially develops **concept of scanning electron microscope**

**Ernst Ruska (1906-1998)**

1928 Experimentally demonstrates **electromagnetic focusing**

**Max Knoll (1897-1969) & E. Ruska**

1931 Build the **first transmission electron microscope** (Berlin)

*Receives Nobel Prize… in 1986! “Conventional” TEM, not SEM…

1930’s Other electron microscope built in England, Belgium, USA and Canada
Johann and Cauchois
1931  SEM-focusing spectrometers by bending multilayer structures.

Johansson
1932  Focusing spectrometer by bending a crystal to twice the radius of the focusing circle, then grinding to achieve full focus.

Manfred von Ardenne (1907-1997)
1938  Credited with developing the first scanning electron microscope

Vladimir Zworykin (1888-1882), James Hillier (1915-2007) & R.L. Snyder
1942  First thick specimen SEM at RCA labs

James Hillier (1915-2007)
1943  Develops concept for electron probe microanalysis – The use of a focused electrons impinging on a specimen and their utility in chemical characterization.

Technique patented in 1947 but working model never constructed...

Raimond Castaing (1921-1998) *
1949-51  Develops concept for electron-probe, X-ray microanalysis (using characteristic X-rays for chemical analysis), and builds the first electron microprobe in Paris.

1949  First commercial TEM had been introduced by Philips Electron Optics.
1956  First commercial microprobe from Cameca, following Castaing’s work
1965  First commercial SEM is offered by Cambridge Instruments

First commercial SEM (Cambridge Inst.)

Stereoscan Mark IV (SEM, Cambridge Inst.) delivered to NASA in 1967

1960s brought expansion of electron microprobe technology and commercial availability:

➤ Cameca
➤ JEOL (& Shimadzu)
➤ Cambridge Instruments
➤ Advanced Metals Research
➤ Applied Research Laboratories
➤ Elion Instruments
➤ Materials Analysis Company
➤ Hitachi

Only Cameca and JEOL offer dedicated electron microprobes today…
The “father” of the electron microprobe...

Raymond Castaing
(1921-1998)
Many commercial SEMs today:

- JEOL (Japan Electron Optics Lab)
- Hitachi
- Carl Zeiss
  - 1990: Wild Leitz + Cambridge Instruments = Leica
  - 1995: Carl Zeiss + Leica = LEO
  - 2004: LEO integrated into Carl Zeiss
  - 2006: Carl Zeiss acquires ALIS
- FEI
  - FEI and Philips Electron Optics merge 1997
  - FEI acquires Micron 1999
- Tescan
- Camscan
- Topcon / ISI
SEM technology today

Ultra-high resolution
(now to 0.4-0.5nm, Hitachi S-5500)
- Cold field emission
- Schottky emission
- Variable pressure

SEM technology today:
- Extreme high resolution
- Sub nm image resolution for full voltage range
- Analytical current capability
  (FEI Magellan)
- Energy filtered Schottky emission
### Electron BackScatter Diffraction (EBSD)

- **1928**  
  S. Nishikawa and S. Kikuchi discovered diffraction pattern (black and white lines in pairs) using grazing incidence beam (6°) = “Kikuchi bands (pattern).”

- **1969-79**  
  Discovery of Selected Area Channeling Pattern (SACP). Kossel diffraction and EBSD.

- **1986**  
  N. Schmidt wrote the first software to index SACP

- **1986-90**  
  Commercialization of the first EBSD systems by Link Analytical (now Oxford Inst.) and HKL Technology

Quartz orientation map

### Helium ion microscope – ultra high resolution microscopy (ALIS ~ 2005)

- **FOV ~12μm**
- **FOV ~4.5μm**

- **FOV ~1μm**
- **FOV ~0.2μm**

*FOV = field of view*
Helium ion microscope – Resolution

Wavelength of He⁺ (or other ion, such as Ga⁺) is 1% or less than electron wavelength.

Hence a smaller resolving power / better resolution can be achieved!

Combined FIB / SEM (dual beam)

Applications...
- Preparing samples for TEM or atom probe
- Reconstructing 3D images from slicing and imaging sequence
**Atom Probe tomography (APT)**

1967  Invented by E.W. Müller, J.A. Panitz, & S.B. McLane.

1974  Invention of Imaging Atom Probe (IAP) by J.A. Panitz. Ions extracted from a nm-scale tip; by accelerating and locating them on a “screen”, location and atom mass (function of the “time of flight”) can be determined.

2006  Commercial instrument by Cameca with laser pulsing to extract atoms even in insulators (geological materials!)
The synergistic approach:
EPMA + FIB + APT