Lecture-13

Characterization of Nanomaterials

(SAXS, SEM)

(Ref: Guozhong Cao; Nanostructures & Nanomaterial: Synthesis, Properties & Applications)

Small angle X-ray scattering (SAXS)

- SAXS is another powerful tool in characterizing

  - Nanostructured Materials

- Strong diffraction peaks result from

  - Constructive interference of X-rays scattered

    (From ordered arrays of Atoms & Molecules)

- Lot of information can be obtained from

  - Angular distribution of scattered intensity (Low angles)

- Fluctuations in electron density over lengths (> 10nm)

  - Can be sufficient to produce an appreciable

    scattered X-ray intensities at angles $2\theta < 5°$

- These variations can be from differences in

  - Density, Composition or from Both, and

  - Do not need to be periodic.

- Amount & Angular Distribution of Scattered Intensity provides various information, such as:

  - Size of very small particles or

  - Surface Area per unit Volume (Crystalline or Amorphous Samples)

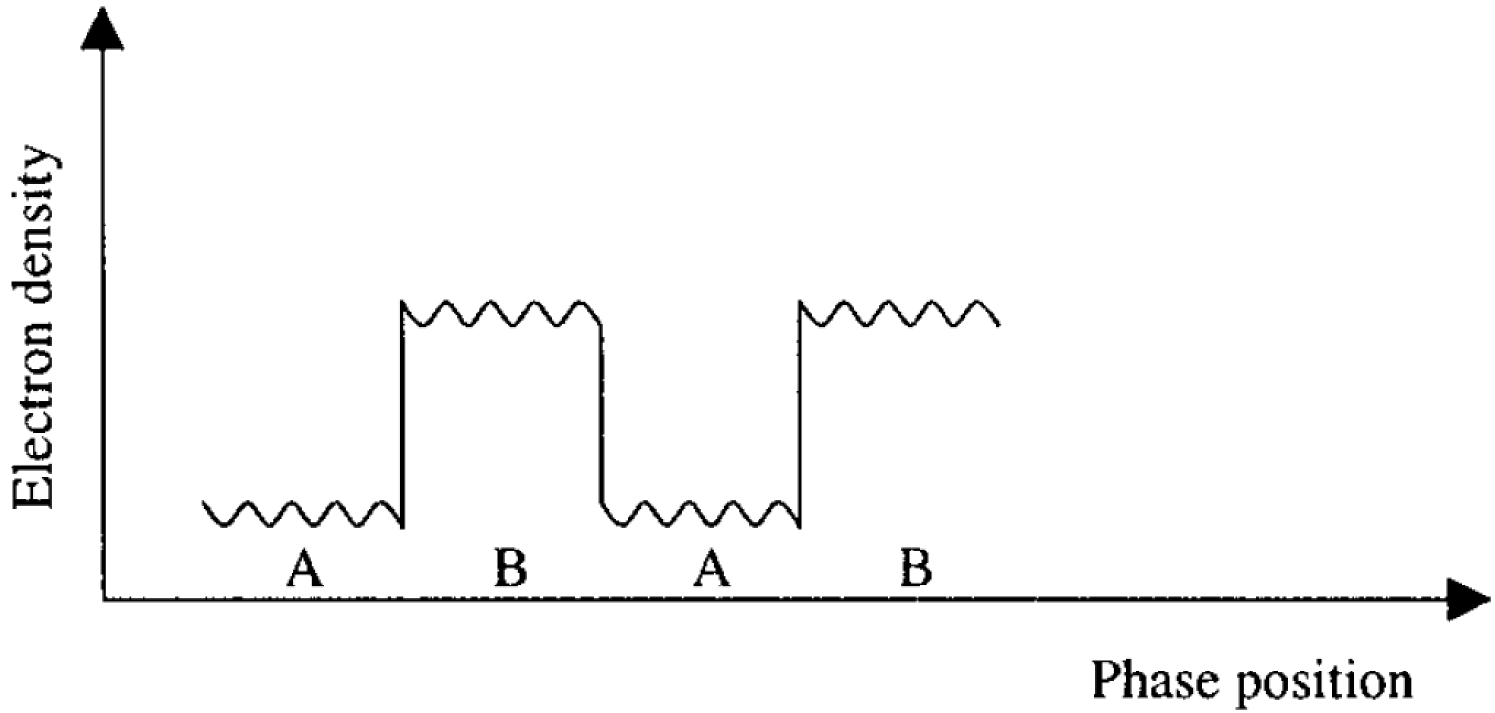
- Let us consider a body with inhomogeneous structure

  - Assuming it consists of two phases

  - Separated by well-defined boundaries

  (such as nanoparticles dispersed in homogeneous medium)

- Electron Density of such a two-phase structure can be schematically described in following figure:



Schematic representing the electron density of a two-phase structure. The variation of electron density can evidently be divided into two categories. The first type is the deviation resulting from the atomic structure of each of the phases, and the second type is due to the heterogeneity of the material.

- The SAXS intensity, I(q), scattered from a collection of

  - Number of noninteracting nanoparticles (N)

  - Having uniform electron density (ρ)

  - In homogeneous medium of electron density (ρ_0)

  can be expressed as:

$$I(q) = I_0 N(\rho-\rho_0)^2 F^2(q)$$

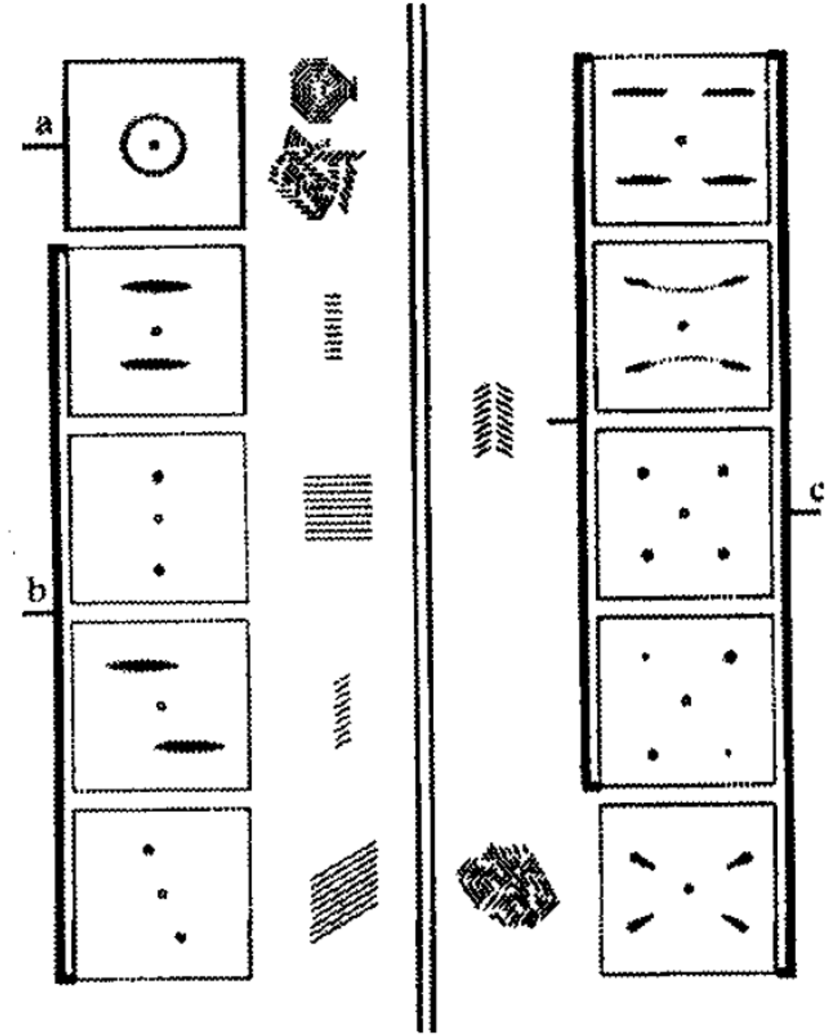
- I_0 is the incident X-ray intensity, and
- F(q) is the form factor - (Fourier Transform of the shape of scattering object)
- For spheres of radius, R, the form factor is expressed by

$$F(q) = 4\pi R^3 \left\{ \frac{\sin(qR) - qR\cos(qR)}{(qR)^3} \right\}$$

where; $q = \frac{4\pi \sin(\theta/2)}{\lambda}$,

λ is the X-ray wavelength,

θ is angle between primary & scattering X-ray beam.



Schematic of long range ordered structures and corresponding diffraction patterns in the small angle region. (a) A ring pattern corresponds to spherically symmetric assemblies of crystallites or unoriented stacks of lamellar crystallites. (b) Two-point/line patterns reveal the oriented stacks of lamellar crystallites. (c) Four-point/line patterns indicate lamellar crystallites stacked in two different orientation.

Ref.: B.D. Cullity & S.R. Stock, Elements of X-Ray Diffraction, 3rd Edition, Prentice Hall, Upper Saddle River, NJ, 2001.

- Apparatus for measuring the distribution of small angle scattering generally employ:
    - Transmission geometry
    - Using fine monochromatic radiation beam
- SAXS permits the measurement of:
    - Size inhomogeneity regions (1 to 100 nm).

- Wide applications of SAXS, varying from

  - Biological Structures

  - Porosity in coals

  - Dispersoids in structural engineering materials

- Theory of visible light scattering is identical to SAXS

  - If the following condition is met:

$$\frac{8\pi R(n_1 - n_2)}{n_2 \lambda} \ll 1$$

  where; n_1 and n_2 are the refractive indices of a particle and its environment, respectively.

- Visible light scattering is limited to systems (R>80 nm)

Scanning Electron Microscopy (SEM)

- SEM is most widely used techniques to characterize

  - Nanomaterials & Nanostructures

- Resolution of SEM approaches a few nanometers

- Instruments magnifications are easily adjusted from

  - 10 to over 300,000

- SEM produce topographical information
  - Similar to optical microscopes
- It also provides the information about
  - Chemical composition near the surface

- A source of electrons is focused into a beam,
  - With a very fine spot size of -5 nm and
  - Having energy (few hundred eV to 50 KeV)
- Beam is rastered over the surface of specimen
  - By deflection coils

- As the electrons strike & penetrate the surface
    - Number of interactions occur resulting in
    - Emission of electrons & photons from sample
- SEM images are produced by collecting the
    - Emitted electrons on cathode ray tube (CRT)

- Various SEM techniques are differentiated on the basis of what is subsequently detected and imaged
- Principle images produced in SEM are of 3 types:

  - Secondary Electron Images
  - Back Scattered Electron Images, and
  - Elemental X-ray Maps

- When high-energy primary electron interacts with atom, either
    - It undergoes inelastic scattering with atomic electrons or
    - Elastic scattering with atomic nucleus.
- In an inelastic collision with an electron, the primary electron
    - Transfers part of its energy to other electron.
- When the energy transferred is large enough,
    - Other electron will emit from the sample.

- If energy of emitted electron < 50 eV

  - It is referred as secondary electron.

- Backscattered electrons are high energy electrons that are

  - Elastically scattered, and

  - Possess same energy as incident or primary electrons.

- The probability of backscattering increases with the

  - Atomic number of the sample material.

- Backscattering images cannot be used for

    - Elemental Identification

- Useful contrast can develop between regions of

    - Specimen that differ in atomic number, Z

- An additional electron interaction in SEM is that:

    - Primary electron collides with core electron

    - Ejects core electron from atom of sample

- Excited atom will decay to its ground state by either

    - Emitting a characteristic X-ray photon; or

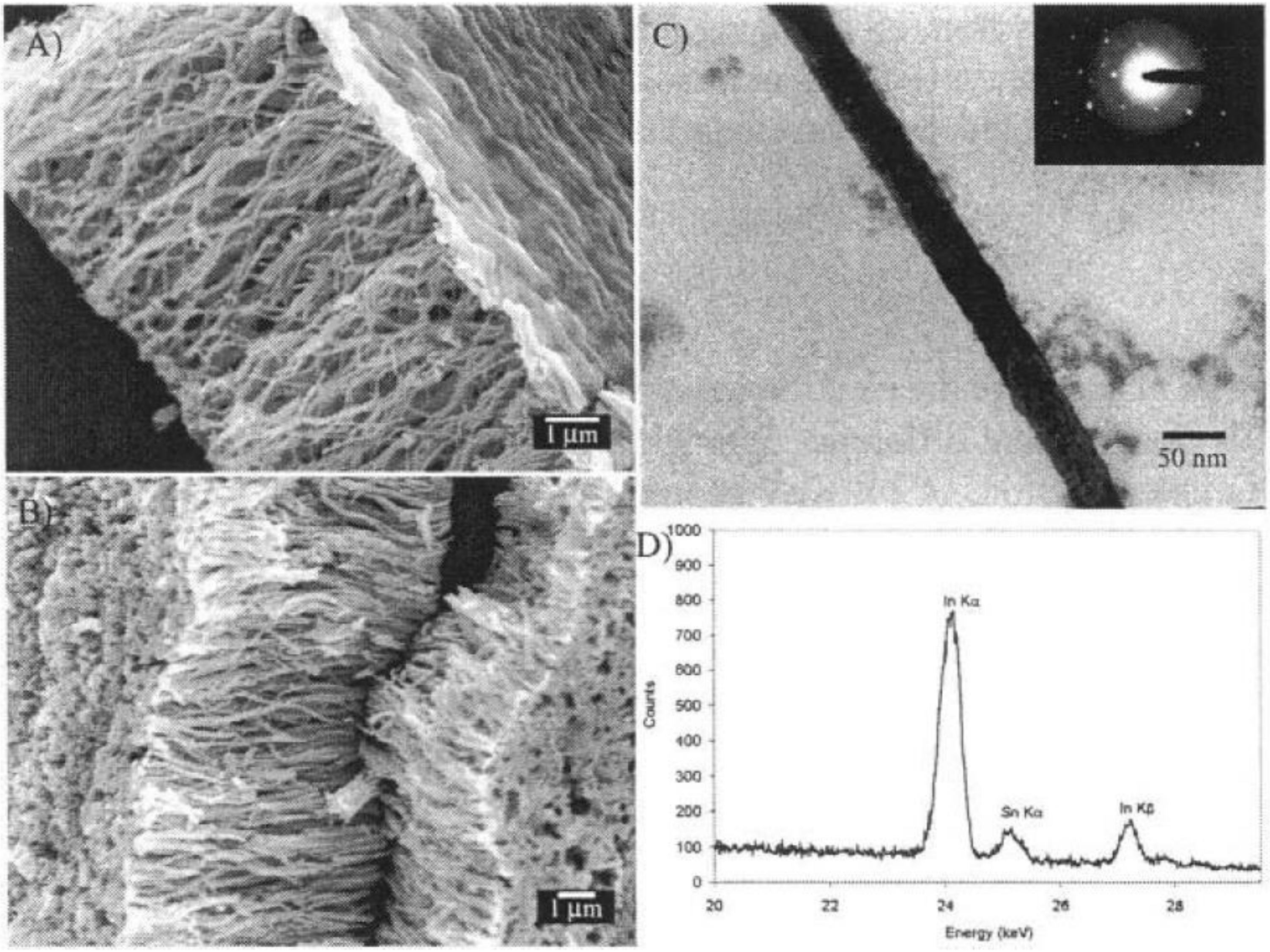
    - An Auger electron

- Both (X-ray photon & Auger Electron) are used for:

    - Chemical Characterization

Combining with chemical analytical capabilities:

- SEM provides image of the
    - Morphology & Microstructures of
    - Bulk & Nanostructured materials and devices
- It can also provide detailed information of
    - Chemical composition and distribution



(A) and (B) SEM images of nanorod arrays, (C) TEM image with electron diffraction pattern, and (D) the EDS spectrum of indium doped tin oxide (ITO) grown by template-based sol-gel electrophoretic deposition.

Ref.: S.J.Limmer, S.Vince Cruz, and G.Z.Cao.

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Course Name: Nano Materials and Applications
Course Code: PHYS3024