Lecture-12
Characterization of Nanomaterials

(Structural Characterization, XRD)

(Ref: Guozhong Cao; Nanostructures & Nanomaterial: Synthesis, Properties & Applications)
Characterization and Properties of Nanomaterials

- Nanomaterials & Nanostructures are characterized by:

  - X-ray diffraction (XRD)

  - Various Electron Microscopy (EM)

    (i) Scanning Electron Microscopy (SEM)

    (ii) Transmission Electron Microscopy (TEM)

    (iii) Scanning Probe Microscopy (SPM)
• Chemical Characterization Techniques
  - Optical Spectroscopy
  - Electron Spectroscopy
  - Ionic Spectrometry

• Relationships between physical properties and Dimensions of nanomaterials are briefly discussed.
Structural Characterization

• Characterization of nanomaterials/nanostructures
  - Surface Analysis Techniques, &
  - Conventional Characterization Methods

• Similar to methods developed for bulk materials.
Example:

For nanoparticles, nanowires and thin films:

• XRD has been widely used for

  - Determination of Crystallinity

  - Crystal Structures, and

  - Lattice Constants
• SEM & TEM together with Electron Diffraction
  - Used in characterization of Nanoparticles.
• Optical spectroscopy is used to determine
  - Size of Semiconductor Quantum Dots.
• SPM is relatively new characterization technique
  - Found wide applications in Nanotechnology.
• Two major members of SPM family are
  - Scanning Tunneling Microscopy (STM)
  - Atomic Force Microscopy (AFM)

• STM & AFM are surface image techniques & can produce
  - Topographic Images of surface
  - Atomic resolution in all three dimensions
  - Combining with appropriately designed attachments
• STM & AFM have broadened range of applications
  - Nanoindentation
  - Nanolithography
  - Patterned Self-Assembly.

• Almost all solid surfaces, can be studied with STM & AFM
  - Whether Hard or Soft
  - Electrically Conductive or non-Conductive

• Surfaces can be studied in Air or Vacuum or Liquid.
X-ray diffraction (XRD)

• XRD is very important techniques to address issues
  
  - Related to Crystal Structure of Solids
  - Lattice Constants and Geometry
  - Identification of Unknown Materials
  - Orientation of Single Crystals
  - Preferred Orientation of Polycrystals
  - Defects, Stresses, etc.
Bragg’s Law

• X-rays ($\lambda = 0.7\text{-}2 \text{ Å}$), incident on specimen, &
  - Diffracted by crystalline phases of specimen
  - In accordance to Bragg's law:

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

‘$d$’ is spacing between atomic planes

‘$\lambda$’ is X-ray wavelength.
• Intensity of diffracted X-rays is measured as
  - Function of the diffraction angle $2\theta$, &
  - Specimen’s Orientation.
• Diffraction Pattern is used to identify
  - Specimen’s Crystalline Phases, &
  - To measure its structural properties.
• Diffraction peak positions are accurately measured with XRD
  - Best method to characterize
    (a) Homogeneous Strains
    (b) Inhomogeneous Strains.

• Homogeneous or Uniform Elastic Strain
  - Shifts the diffraction peak positions.

• From shift in peak positions, one can calculate
  - Change in d-spacing (Occurs due to change of lattice constants under strain)
• Inhomogeneous strains vary from
  - Crystallite to Crystallite

  or

  - Within a single crystallite

• This causes broadening of diffraction peaks &
  - Increases with sin \( \theta \).
• Peak broadening is also caused by
  - Finite size of crystallites

• Here the broadening is independent of $\sin \theta$

• When both crystallite size & inhomogeneous strain
  - Contribute to the peak width

• It can be separately determined by
  - Careful analysis of peak shapes
If there is no In-Homogeneous strain,

- Crystallite size, ‘D’, can be estimated from peak width

- Using Scherrer's formula:

\[ D = \frac{K \lambda}{B \cos \theta_B} \]

Where; ‘\( \lambda \)’ is the X-ray wavelength

‘B’ is full width half maximum (FWHM) (Diffraction Peak)

‘\( \theta_B \)’ is the diffraction angle, and

‘K’ is the Scherrer’s constant (Order of unity for usual crystal)
- Nanoparticles often form twinned structures
- Therefore, Scherrer’s formula may produce results different from the true particle sizes.
- In addition, X-ray diffraction only provides collective information of the particle sizes, &
  - Usually requires a sizable amount of powder.
• It should be noted that estimation would work
  - Only for very small particles

• Technique is very useful in
  - Characterizing nanoparticles

• Similarly, film thickness can also be estimated for
  - Epitaxial & highly textured thin films with XRD
Powder X-ray diffraction of a series of InP nanocrystal sizes. The stick spectrum gives the bulk reflections with relative intensities.

• Disadvantages of XRD, (Compared to Electron Diffraction)
  - Low intensity of diffracted X-rays
  - Particularly for low-Z materials
• XRD is more sensitive to high-Z materials
• For low-Z materials
  - Neutron or Electron diffraction is more suitable
• Typical intensities for Electron Diffraction are
  
  - $10^8$ times larger than XRD

  - Because of small diffraction intensities

• XRD generally requires large specimens

• Information acquired is an average over a large amount of material
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