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 (λ= 0.7-2 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

'λ' is X-ray wavelength.

- Intensity of diffracted X-rays is measured as

  - Function of the diffraction angle 2θ, &

  - 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 θ.

- 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; ‘λ’ is the X-ray wavelength

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

‘θ_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

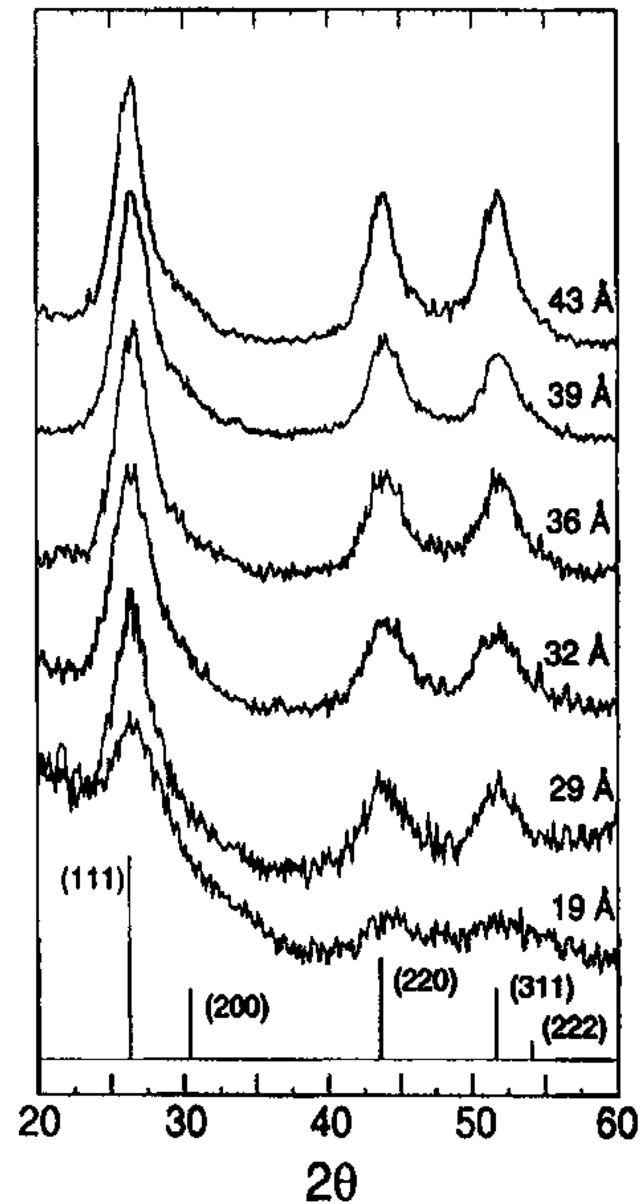
    - Only for very small particles

- 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.
[A.A. Guzelian et.al., J. Phys. Chem., 100(1996)7212]

- 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

Prof. S. K. Tripathi

Department of Physics
School of Physical Sciences
Mahatma Gandhi Central University

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