Lecture-14
Characterization of Nanomaterials

(TEM, SPM)

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

Transmission Electron Microscopy (TEM)

- In TEM, electrons are accelerated to

    - 100 KeV or higher (up to 1 MeV),

- Projected on thin specimen (< 200 nm) by means of:

    - Condenser lens system

- Penetrate the sample thickness either

    - Undeflected or Deflected.

- Advantages that TEM offers:

  - High Magnification ranging from 50 to 10^6, &

  - From single sample, ability to provide both

    (a) Image Information, &

    (b) Diffraction Information

- Scattering processes experienced by electrons
    - During their passage through specimen
    - Determine the kind of information obtained
- Elastic scattering involves
    - No energy loss, and
    - Gives rise to diffraction patterns

- Inelastic interactions between primary & sample electrons at heterogeneities:

  (Grain Boundaries, Dislocations, Second-phase Particles, Defects, Density Variations, etc.)

  - Cause complex absorption & scattering effects

- It leads to spatial variation in intensity of transmitted electrons.

- In TEM imaging process, one can easily switch between

  - Imaging the sample, and

  - Viewing its diffraction pattern

  by changing strength of the intermediate lens

- Higher magnification (resolution) of TEM image is due to small effective electron wavelengths, λ, given by De-Broglie relationship:

$$\lambda = \frac{h}{\sqrt{2mqV}}$$

Where; m and q are the electron mass & charge, h is Planck's constant, and V is the potential difference by which electrons are accelerated.

- For example, electrons of 100 KeV energy, λ =0.37 nm are capable of transmitting through ~ 0.6 μm of silicon.
- Higher the operating voltage of a TEM instrument,
  - Greater its lateral spatial resolution.
- Theoretical instrumental point-to-point resolution is
  - Proportional to $\lambda^{3/4}$

- High-voltage TEM instruments (with e.g. 400 KV) have

    - Point-to-Point resolutions better than 0.2 nm.

- High-voltage TEM have additional advantage of

    - Greater electron penetration

- High-energy electrons interact less strongly with matter than lower energy electrons.

- On high voltage TEM, it is possible to work with
    - Thicker Samples
- Shortcoming of TEM is
    - It’s limited Depth Resolution
- Electron scattering information in a TEM image
    - Originates from a three dimensional sample, &
    - It is projected on a two-dimensional detector.

- Therefore, structure information along the electron beam direction is superimposed at the image plane.
- Most difficult aspect of TEM technique is

  - Preparation of samples

  - It is less so for nanomaterials.

- Selected-Area Diffraction (SAD) offers a unique capability to determine the crystal structure of

    - Individual nanomaterials

    - Such as nanocrystals and nanorods

    - Crystal structures of different parts of sample.

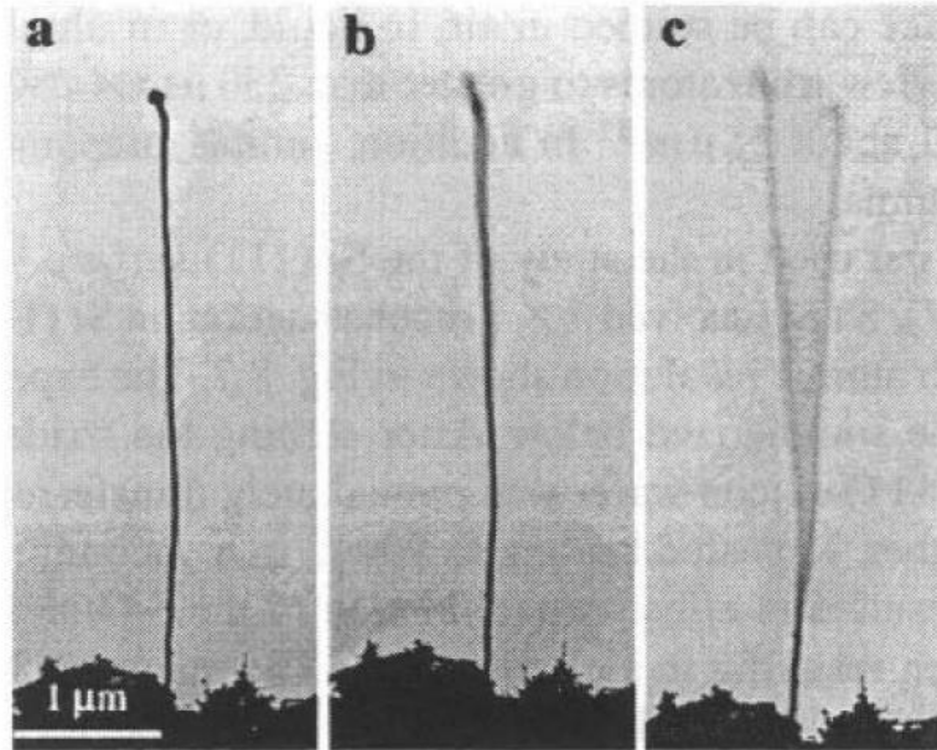
- In SAD, the condenser lens is defocused
    - To produce parallel illumination at specimen
- Selected-area aperture is used to limit
    - Diffracting Volume
- SAD is used for crystalline materials to determine:
    - Bravais lattices and lattice parameters
    - Similar to the procedures used in XRD.

- TEM has no inherent ability to distinguish atomic species.
- Electron scattering is sensitive to the target element.
- Various spectroscopy are developed for
  - Chemical composition analysis
- Examples include
  - Energy-dispersive X-ray Spectroscopy (EDS), and
  - Electron Energy Loss Spectroscopy (EELS).

- TEM has been explored for applications in nanotechnology.
- Examples include;
  - Determination of melting points of nanocrystals
- An electron beam is used to heat up the nanocrystals, and
- Melting points are determined by the
  - Disappearance of electron diffraction.

- Another example is the measurement of mechanical and electrical properties of individual nanowires and nanotubes.
- The technique allows a one-to-one correlation between structure & properties of the nanowires.

Figure shows TEM micrographs of a silicon nanowire when stationary and vibrating at resonance from which the Young's modulus of this silicon nanowire is determined.



(A) Selected Si nanowires at (a) stationary, (b) the first harmonic resonance with the vibration plane parallel to the viewing direction, and (c) the resonance with the vibration plane perpendicular to the viewing direction. A slight difference in the resonance frequencies in (b) and (c) results from the anisotropic structures of the nanowire.

Ref.: Z.L.Wang, Adv. Mater. 12(2000)1295

Scanning Probe Microscopy (SPM)

- SPM is unique among imaging techniques, by providing

    - Three-dimensional (3-D) real-space images

- Other analysis techniques allows spatially localized measurements of structure and properties.

  (In optimum conditions subatomic spatial resolution is achieved)

- SPM is a general term for a family of microscopes depending on the probing forces used.

- Two major members are STM and AFM.

- STM was first developed by

    - Binnig and his coworkers in 1981

- AFM was invented a few years later

- The limitation of STM, is restricted to

    - Electrically conductive sample surface

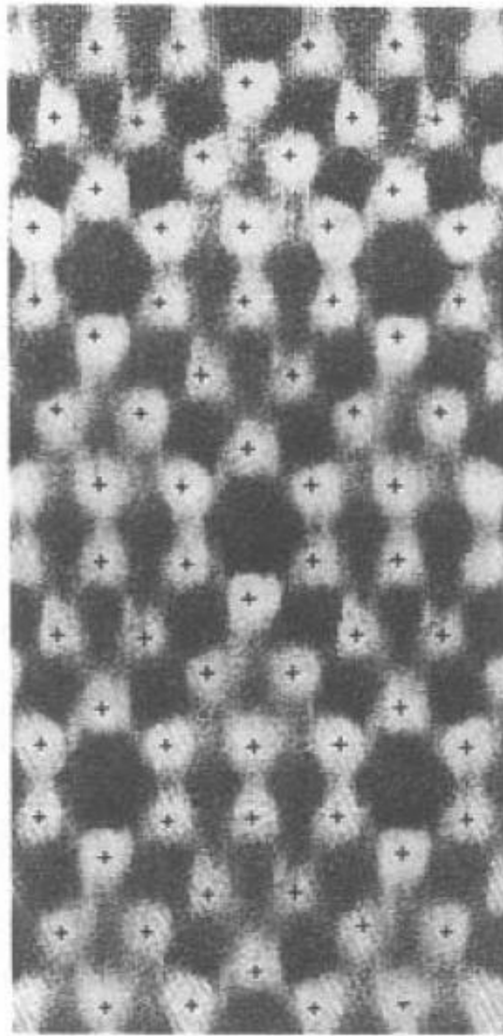
- It is complemented by AFM, which does not require

    - Conductive sample surface

- Almost any solid surface can be studied with SPM:
  - Insulators, Semiconductors and Conductors
  - Magnetic, Transparent and Opaque Materials.
- In addition, surface can be studied
  - In air, liquid, or in ultrahigh vacuum
  - Fields of view from atoms to > 250μm x 250μm
  - Vertical ranges of about 15μm.
- Sample preparation for SPM analysis is minimal.

- STM was first used in the study of Si (111) surface
- In ultrahigh vacuum (UHV), STM resolved 7x7 reconstruction on Si (111) surface in real space
- The experimental procedures can be summarized as:
- After etching the oxide with an HF solution,

  - (111) silicon wafer was immediately transferred
  - To the STM in UHV chamber.

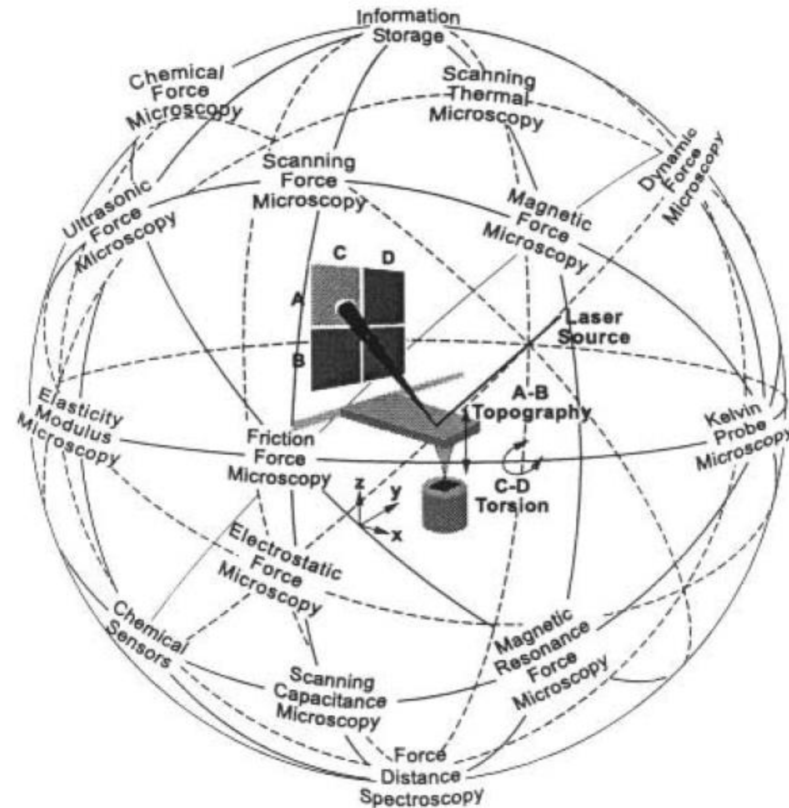


(a) STM image of 7x7 reconstruction on Si (111) surface in real space with atomic resolution. (b) Modified adatom model. The underlying top-layer atom positions are shown by dots, and the remaining atoms with unsatisfied dangling bonds carry circles, whose thickness indicates the measured depth. The adatoms are represented by large dots with corresponding bonding arms. The empty potential adatom position is indicated by an empty circle in the triangle of adjacent rest atoms. The grid indicates the 7x7 unit cells.

Ref.: G.Binning, H.Rohrer, C.Gerber, and E.Weibel, Phys. Rev. Lett. 50(1983)120.

- Repeated heating to 900°C in a vacuum not exceeding $3x10^{-8}$ Pa resulted in effective sublimation of the SiO layer grown during the transfer, resulting in a clean surface.
- The micrographs were taken at 2.9 V with tip positive.
- Only unidirectional scans were recorded to avoid nonlinear effects of the scanning piezoelectric drives.

- SPM has been developed to a wide spectrum of techniques using various probe and sample surface interactions, as shown in Fig.



SPM consists of a wide spectrum of techniques using various probe and sample surface interactions.

Ref.: H.P.Lang, M.Hegner, E.Meyer, and Ch.Gerber, Nanotechnology, 13(2002)R29.

- The interaction force may be the inter-atomic forces within
    - Atoms of the tip & those of a surface
    - Short-range Van der Waals forces
    - Long-range capillary forces
    - Stick-Slip processes producing friction forces.
- Modifying the tip chemically allows various properties of the sample surface to be measured.
- Depending on type of interactions between tip & sample surface used for the characterization
    - Various types of SPM have been developed.

- Electrostatic force microscopy is based on

    - Local charges on the tip or surface

- It leads to electrostatic forces between

    - Tip and Sample

- Hence, it allows a sample surface to be mapped

  (i.e. Local differences in distribution of electric charge on a surface to be visualized)

- In a similar way, magnetic forces can be imagined

  - If the tip is coated with a magnetic material

- e.g. Iron, that has been magnetized

  - Along the tip axis

- This is called as Magnetic Force Microscopy.

- Tip probes the stray field of the sample &
    - Allows to determine magnetic structure of sample
- When the tip is functionalized as a thermal couple
    - Temperature distribution on sample surface can be measured
- It is called as Scanning Thermal Microscopy.

- The capacity change between tip and sample is evaluated in scanning capacitance microscopy
- Locally resolved measurement of the chemical potential is done by Kelvin probe microscopy.
- Tip can be driven in an oscillating mode to probe
  - Elastic properties of a surface
  - It is referred as Elastic Modulus Microscopy

- At high oscillation frequencies (cantilevers with high resonance frequency), further information on

  - Inter-atomic forces between tip & sample can be obtained

- It is called as Dynamic Force Microscopy.

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