Lahore College for Women University
Lahore

Nanotechnology & Nanostructures (Lecture # 10)

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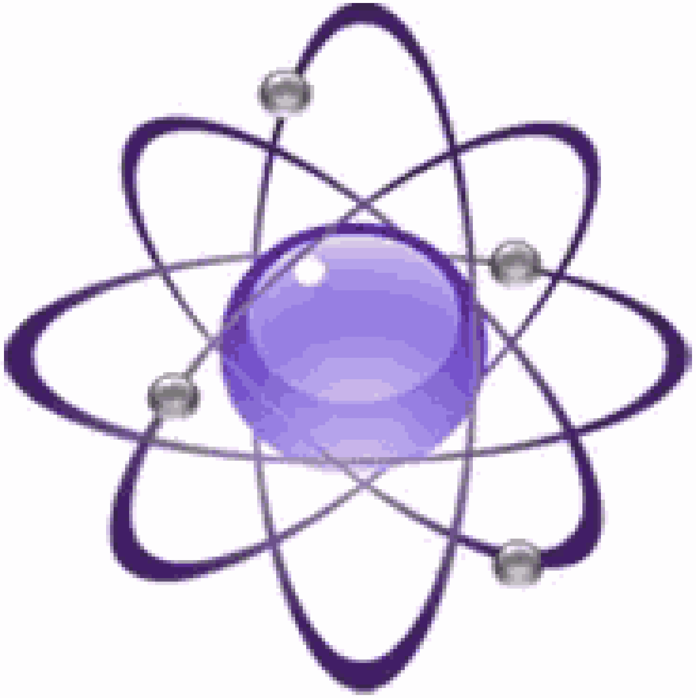
Size Effects:

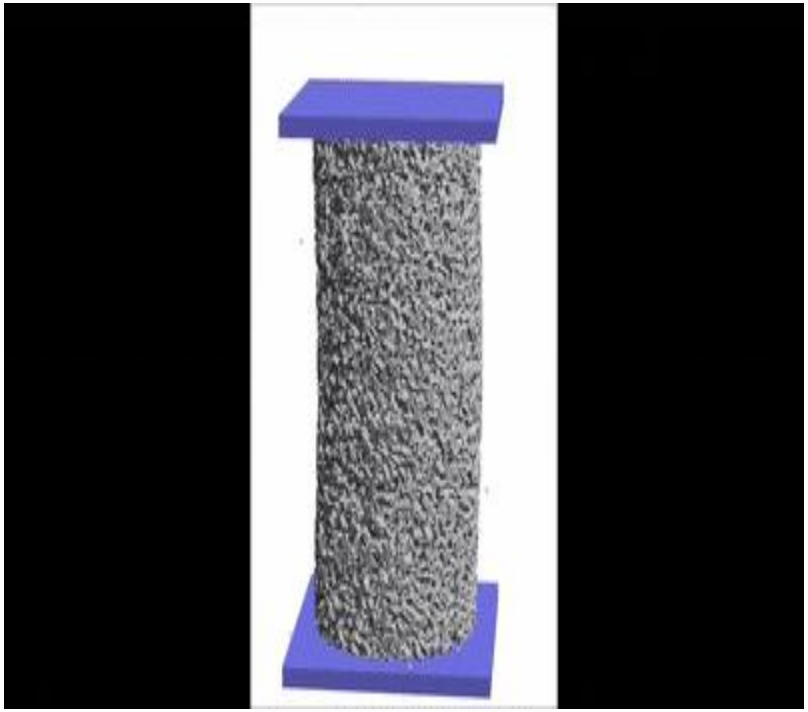
1. Surface-to-Volume Ratio versus Shape
2. Magic Numbers
3. Surface Curvature
4. Strain Confinement
5. Quantum Effects



4. Strain Confinement

❖Planar defects, such as dislocations are also affected when present in a nanoparticle.

❖ Dislocations play a crucial role in plastic deformation, thereby controlling the behavior of materials when subjected to a stress above the yield stress.



In the case of an infinite crystal, the strain energy of a perfect edge dislocation loop is given by:

$$W_S \cong \frac{\mu b^2}{4\pi} \ln\left\{\frac{r}{c}\right\}$$

where
μ = shear modulus.
b = Burgers vector.
r = radius of the dislocation stress field.
c = core cutoff parameter.

•In the nanoscale regime, it is vital to take into account the effect posed by the nearby free surfaces.

•In other words, there are image forces acting on the dislocation half-loop.

• As a consequence, the strain energy of a perfect edge dislocation loop contained in a nanoparticle of size R is given by:

$$W_S \cong \frac{\mu b^2}{4\pi}\left[\ln\left\{\frac{R - r_d}{R}\right\}\right]$$

Where r_d is the distance between the dislocation line and the surface of the particle.

Comparison

- A comparison of Equations reveals that for small particle sizes, the stress field of the dislocations is reduced.

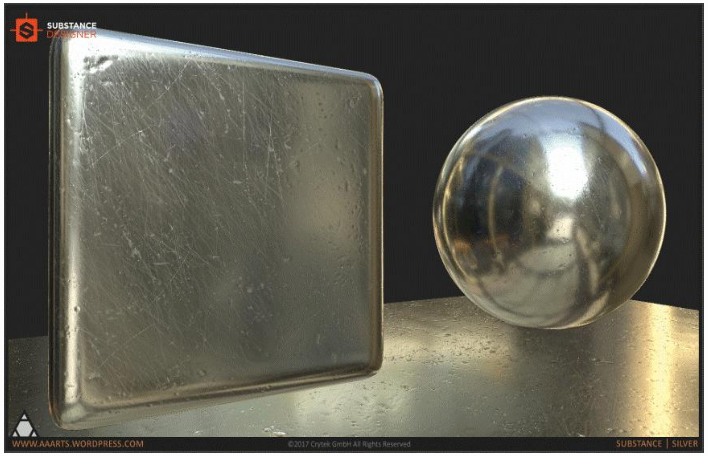
- In addition, the presence of the nearby surfaces will impose a force on the dislocations, causing dislocation ejection toward the nanoparticle’s surface.

- The direct consequence of this behavior is that nanoparticles below a critical size are self-healing as defects generated by any particular process are unstable and ejected.

5. Quantum Effects

- In bulk crystalline materials, the atomic energy levels spread out into energy bands. The valence band, which is filled with electrons, might or might not be separated from an empty conduction band by an energy gap.

- For conductor materials such as metals, there is typically no band gap. Therefore, very little energy is required to bring electrons from the valence band to the conduction band, where electrons are free to flow.



•For insulator materials such as ceramics, the energy band gap is quite significant, and thus transferring electrons from the valence band to the conduction band is difficult.

•In the case of semiconductor materials such as silicon, the band gap is not as wide, and thus it is possible to excite the electrons from the valence band to the conduction band with some amount of energy.

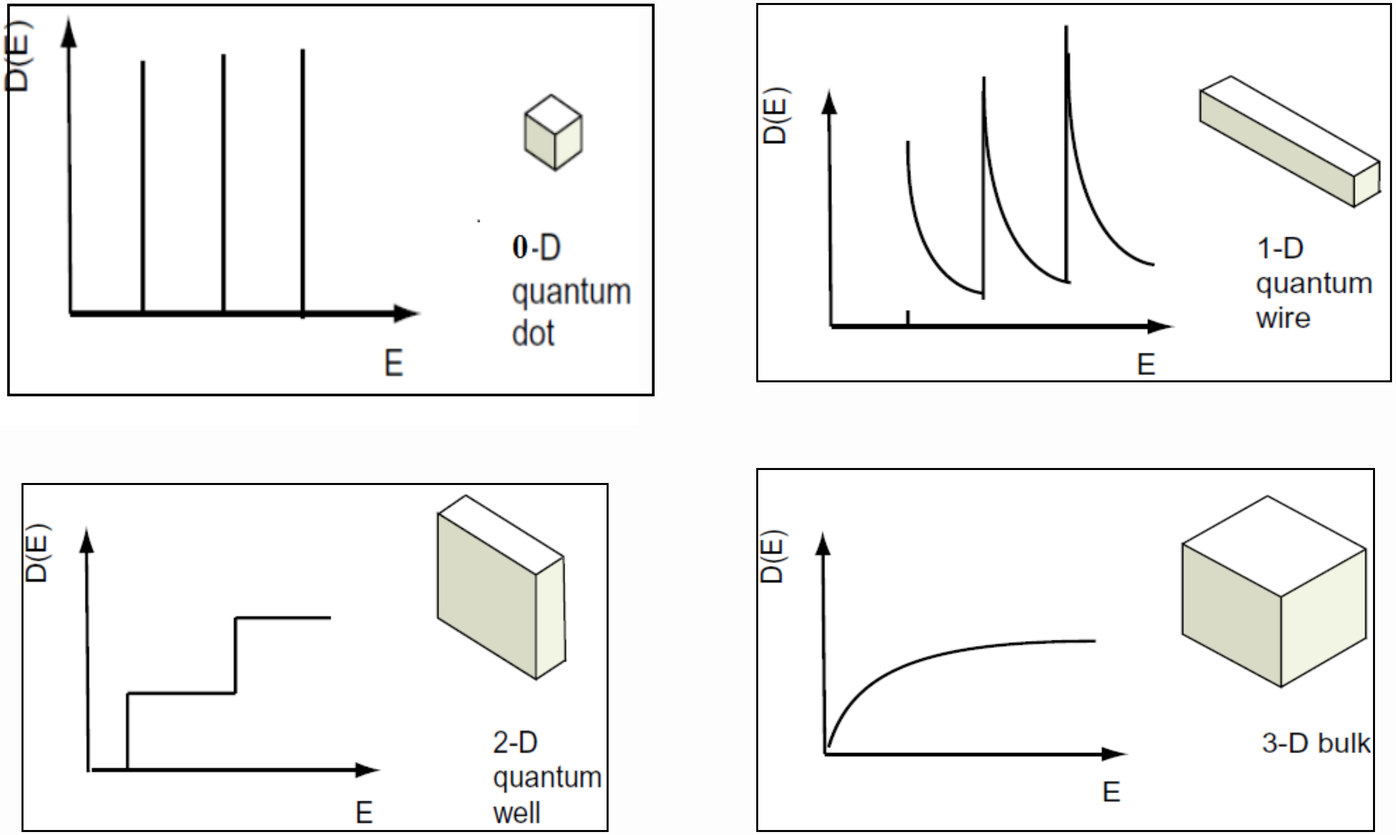
Behavior of bulk crystalline materials through dimensions

- For 0-D nanomaterials, where all the dimensions are at the nanoscale, an electron is confined in 3-D space. Therefore, no electron delocalization (freedom to move) occurs.

- For 1-D nanomaterials, electron confinement occurs in 2-D, whereas delocalization takes place along the long axis of the nano wire/rod/tube.

- For 2-D nanomaterials, the electrons will be confined across the thickness but delocalized in the plane of the sheet.

- For 3-D nanomaterials, the electrons are fully delocalized in all dimensions.



- For 0-D nanomaterials the electrons are fully confined.
- For 3-D nanomaterials the electrons are fullydelocalized.
- In 1-D and 2-D nanomaterials, electron confinement and delocalization coexist.

Effect of confinement by quantum mechanics

- The effect of confinement on the resulting energy states can be calculated by quantum mechanics, as the *“particle in the box”* problem.

- In this treatment, an electron is considered to exist inside of an infinitely deep potential well (region of negative energies), from which it cannot escape and is confined by the dimensions of the nanostructure.

In 0-D, 1-D, and 2-D, the effects of confinement on the energy state can be written respectively as:

(0-D)

$$E_n = \left[\frac{\pi^2\hbar^2}{2mL^2}\right]\left(n_x^2 + n_y^2 + n_z^2\right)$$

(1-D)

$$E_n = \left[\frac{\pi^2\hbar^2}{2mL^2}\right]\left(n_x^2 + n_y^2\right)$$

(2-D)

$$E_n = \left[\frac{\pi^2\hbar^2}{2mL^2}\right]\left(n_x^2\right)$$

where ħ = h/2π, h is Planck's constant, m is the mass of the electron, L is the width (confinement) of the infinitely deep potential well, and n_x, n_y, and n_z are the principal quantum numbers in the three dimensions x, y, and z.

•The smaller the dimensions of the nanostructure (smaller L), the wider is the separation between the energy levels, leading to a spectrum of discrete energies.

• In this fashion, the band gap of a material can be shifted toward higher energies by spatially confining the electronic carriers.

Number of conduction electrons (E_n)

- Another important feature of an energy state E_n is the number of conduction electrons, N (En), that exist in a particular state.

- As E_n is dependent on the dimensionality of the system, so is the number of conduction electrons.

- This also means that the number of electrons dN within a narrow energy range dE, which represent the density of states D (E), i.e., D (E) = dN/dE, is also strongly dependent on the dimensionality of the structure.

- The density of states as a function of the energy E for conduction electrons will be very different for a quantum dot (confinement in three dimensions), quantum wire (confinement in two dimensions and delocalization in one dimension), quantum well (confinement in one dimension and delocalization in one dimension), and bulk material (delocalization in three dimensions.

- Because the density of states determines various properties, the use of nanostructures provides the possibility for tuning these properties.

- For example, photoemission spectroscopy, specific heat, the thermo power effect, excitons in semiconductors and the superconducting energy gap are all influenced by the density of states.

- Overall, the ability to control the density of states is crucial for applications such as infrared detectors, lasers, superconductors, single-photon sources, biological tagging, optical memories, and photonic structures.

Thank you