Nano Sensors

PhD/ MTech/ BTech

Course No.: EEL7450

L-T-P [C]: 3–0–0 [3]

Prof. AJAY AGARWAL

ELECTRICAL ENGINEERING

IIT JODHPUR

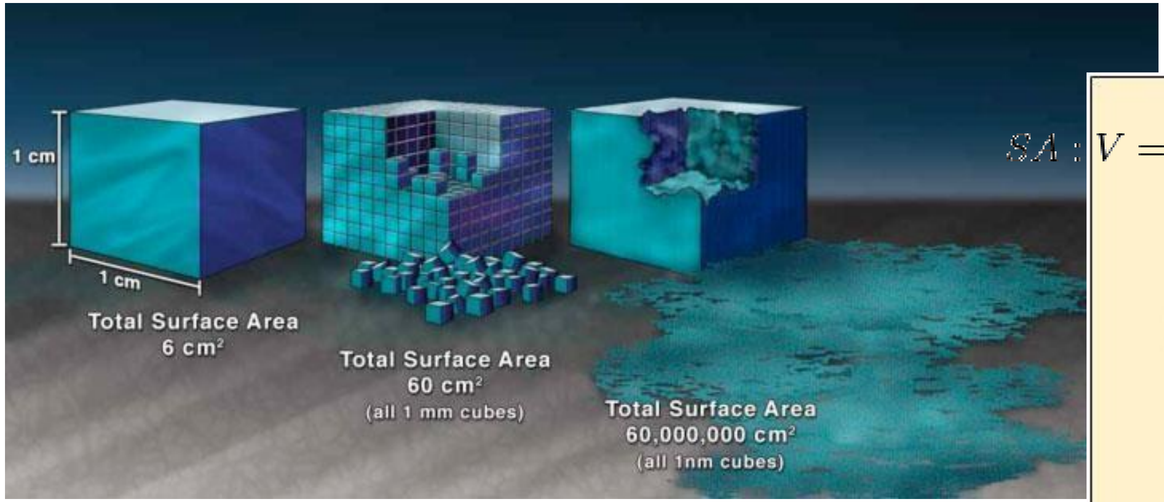
Lecture 04 dated 10^{th} January 2025

Size dependent Properties of nanoscale materials

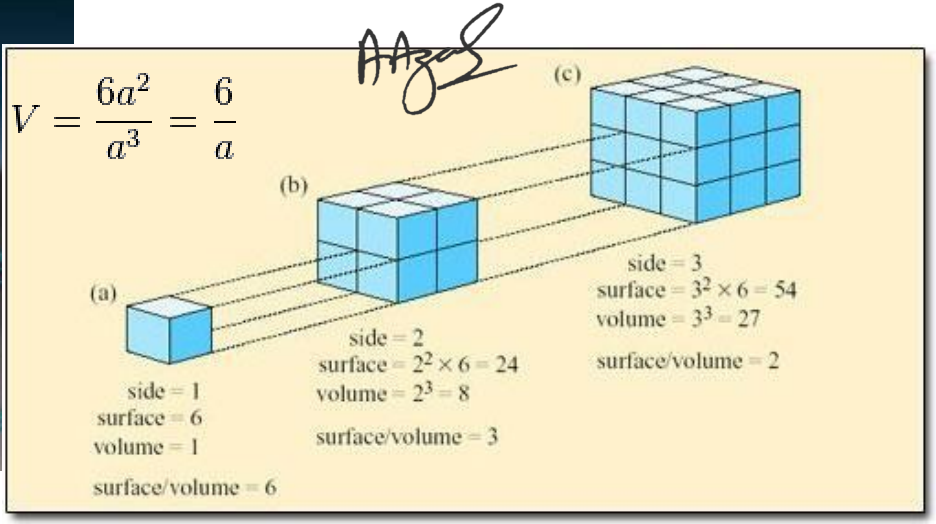
Two principle factors causes the properties of nm differ significantly from bulk material

1. Large Surface effect - Increase in surface area to volume ratio

If a bulk material is divided in smaller particles, the **total volume of material** remains the same, whereas the collective surface area is greatly increased. In other words, the so called surface-to-volume ratio is significantly increased.



$$SA:V = \frac{6a^2}{a^3} = \frac{6}{a}$$



As the particle/ grain size reduces the proportion of atoms exposed on its surface increases

5% for 30 nm particles

20% for 10 nm particles

50% for 3 nm particles

<u>This leads to high chemical reactivity of the nanomaterials</u>

Physical Properties of Nanomaterials

- **Known origins that cause physical properties to change:**
  1. large fraction of surface atoms,
  2. Large surface energy,
  3. Spatial confinement, and
  4. Reduced imperfections

Physical Properties of Nanomaterials

1. **Reduced melting point:** Nanomaterial may have a significantly lower melting point or phase transition temperature and appreciably **reduced lattice constants (spacing between atoms is reduced), due to huge fraction of surface atoms** in the total amount of atoms.
2. **Ultra Hard**: Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of single crystals in the bulk form. The enhancement in mechanical strength is simply **due to the reduced probability of defects**

Physical Properties of Nanomaterials

3. **Optical properties** of Nanomaterials can be significantly different from bulk crystal.
   - Semiconductor Blue shift in adsorption and emission due to an increased band gap – Quantum size effects, Particle in box
   - Metallic Nanoparticles colour changes in spectra due to Surface Plasmons Resonances – Lorentz Oscillator Model
4. **Electrical conductivity** decreases with a reduced dimension due to increased surface scattering

   Electrical conductivity increases due to the better ordering and ballistic transport

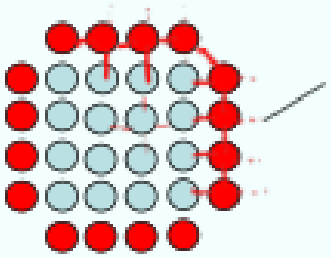
Physical Properties of Nanomaterials

5. **Magnetic properties** of nanomaterials are distinctly different from the bulk materials.
   - Ferromagnetism disappears and transfers to super paramagnetism in the nanometer scale due to the huge surface energy
6. **Self purification** is an intrinsic thermodynamic property of nanostructures and nanomaterials due to enhanced diffusion of impurities/ defects/ dislocations in the nearby surfaces
   - Increased perfection enhances chemical stability

Physical Properties of Nanomaterials

1. Reduced melting point:

Melting points and lattice constants



Nanoparticles of metals,

semiconductors and

molecular crystals

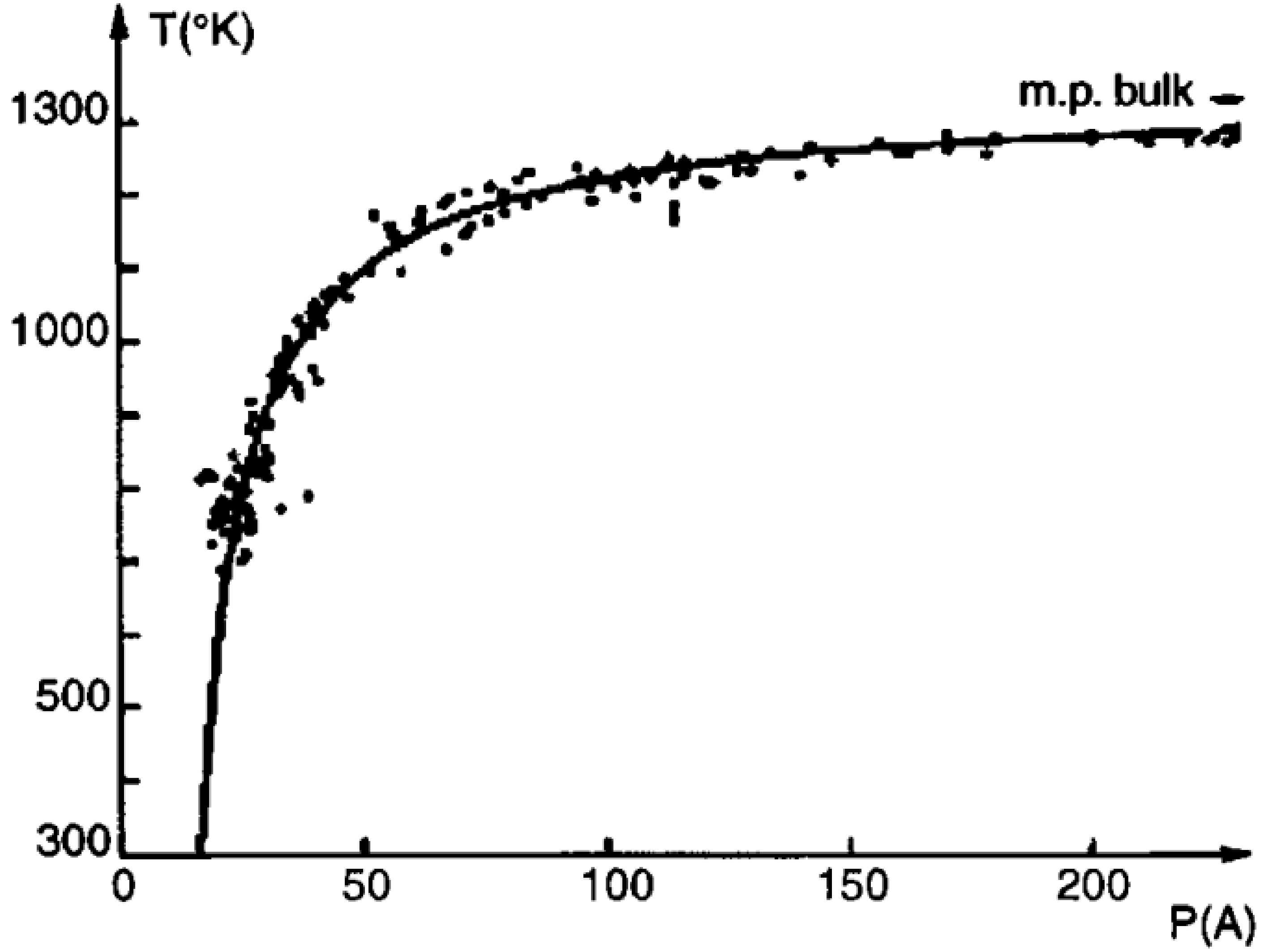
if < 100 nm have a

a lower melting point (the difference can be as large as 1000 deg C) and reduced lattice constant.

Reason:

surface energy to volume energy ratio changes dramatically.

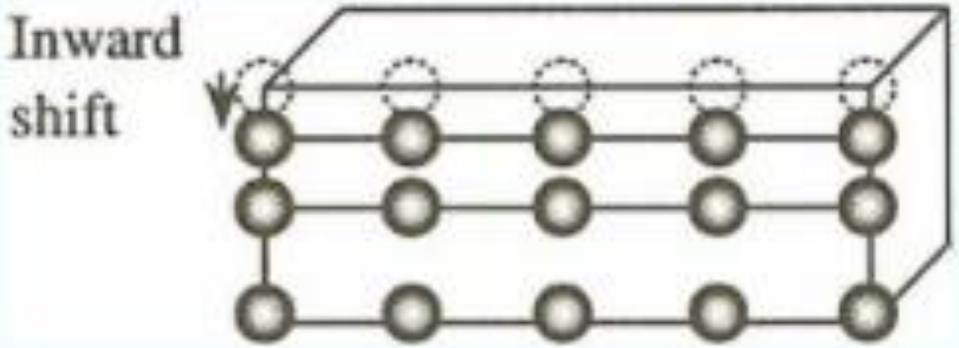
what is easier to get off? surface atom or volume atom.



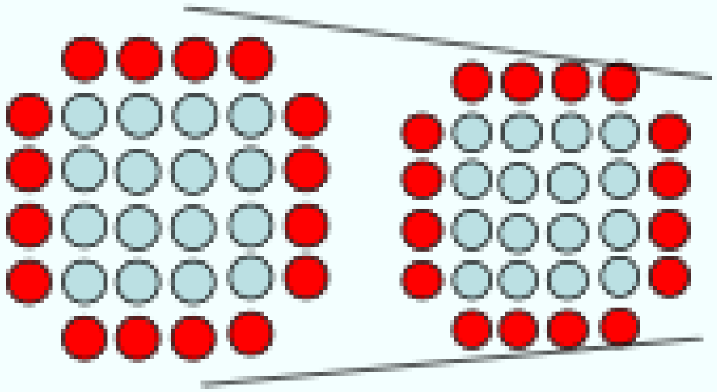
The melting point of bulk gold is of 1337 K and decreases rapidly for nanoparticles with diameters below 5nm. Both experimental data (the dots) and the results theoretical points (the solid line)

Melting points and lattice constants

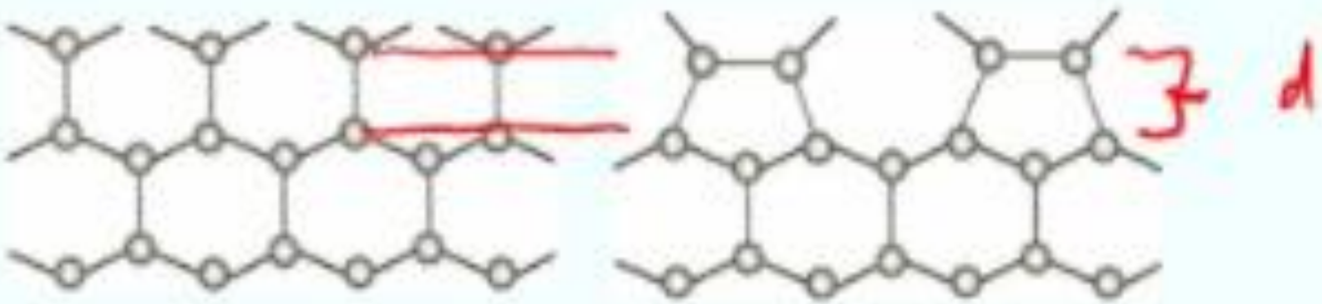
Atoms or molecules on a solid surface possess fewer nearest neighbors or coordination numbers, and thus have dangling or unsatisfied bonds exposed to the surface. Because of the dangling bonds on the surface, surface atoms or molecules are under an inwardly directed force and the bond distance between the surface atoms or molecules and the subsurface atoms or molecules, is smaller than that between interior atoms or molecules.



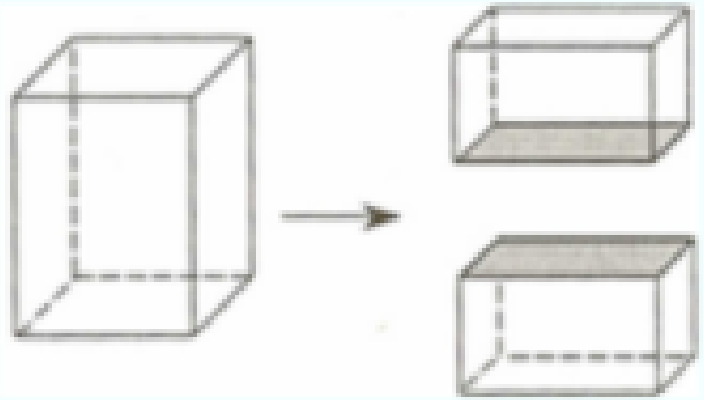
When solid particles are very small, such a decrease in bond length between the surface atoms and interior atoms becomes significant and the lattice constants of the entire solid particles show an appreciable reduction.



surface free energy triggers reconstruction (Example Silicon 100 reconstructs to (2x1)) surface lattice



The extra energy possessed by the surface atoms is described as surface energy, surface free energy or surface tension. Surface energy, γ, by definition, is the energy required to create a unit area of "new" surface:



What is the source of surface free energy?

Concepts of thermodynamics are used to calculate the surface energy of a material.

$$\gamma = \left(\frac{\partial GibbsfreeEnergy}{\partial Area} \right) \Bigg|_{\substack{@ constpressure, \\ temp, number}}$$

Gibbs free Energy is defined as the energy portion of a thermodynamic system available to do work.

$$G = H - TS$$

H is enthalpy, S is entropy and T is the temperature in Kelvin

Enthalpy: a thermodynamic quantity equivalent to the total heat content of a system

Entropy: the unavailability of a system's thermal energy for conversion into mechanical work, often interpreted as the degree of disorder or randomness in the system

Mechanical Properties of Nanomaterials

- they typically improve

The calculated strength of perfect crystals exceeds that of real ones by two or three orders of magnitudes.

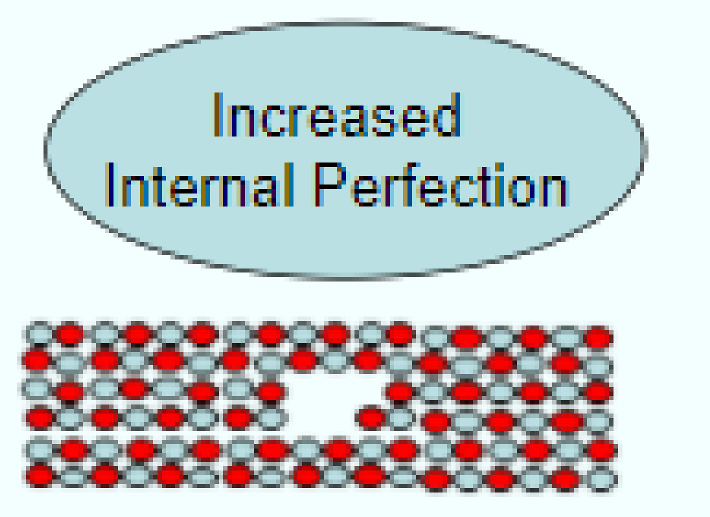
A lot of work has been done on whiskers that approach the theoretical limit first demonstrated by Herring and Galt in 1952 if diameter are less than 10 um.

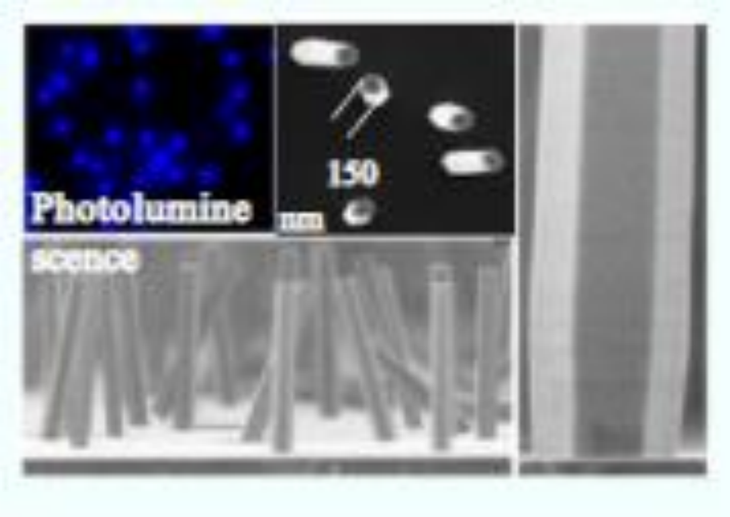
Note: The enhancement starts in the micrometer scale which is different from other size dependent properties.

Two possible mechanisms have been proposed to explain the enhanced strength of nanowires or nanorods (in reality with diameters less than 10 microns).

Increased Internal Perfection

Increased Surface Perfection





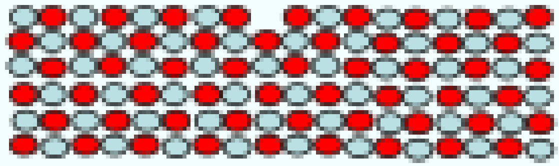
The smaller the cross-section of a whisker or nanowires, the less is the probability of finding in it any imperfections such as dislocations, micro-twins, impurity precipitates, etc

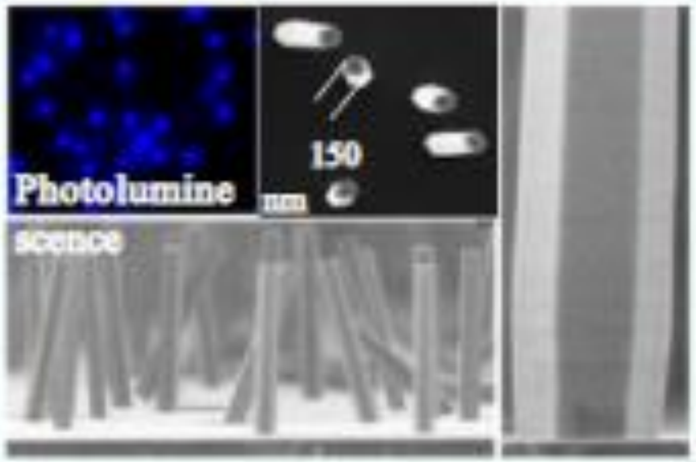
Thermodynamically, imperfections in crystals are highly energetic and can be eliminated -- small sizes makes such elimination of imperfections possible

Imperfections in bulk materials, such as dislocations are often created to accommodate stresses generated in the synthesis and processing of bulk materials due to temperature gradient and other inhomogeneities.

Such stresses can not be excluded but are generally not as likely to exist in small structures, particularly in nanomaterials

Increased Surface Perfection





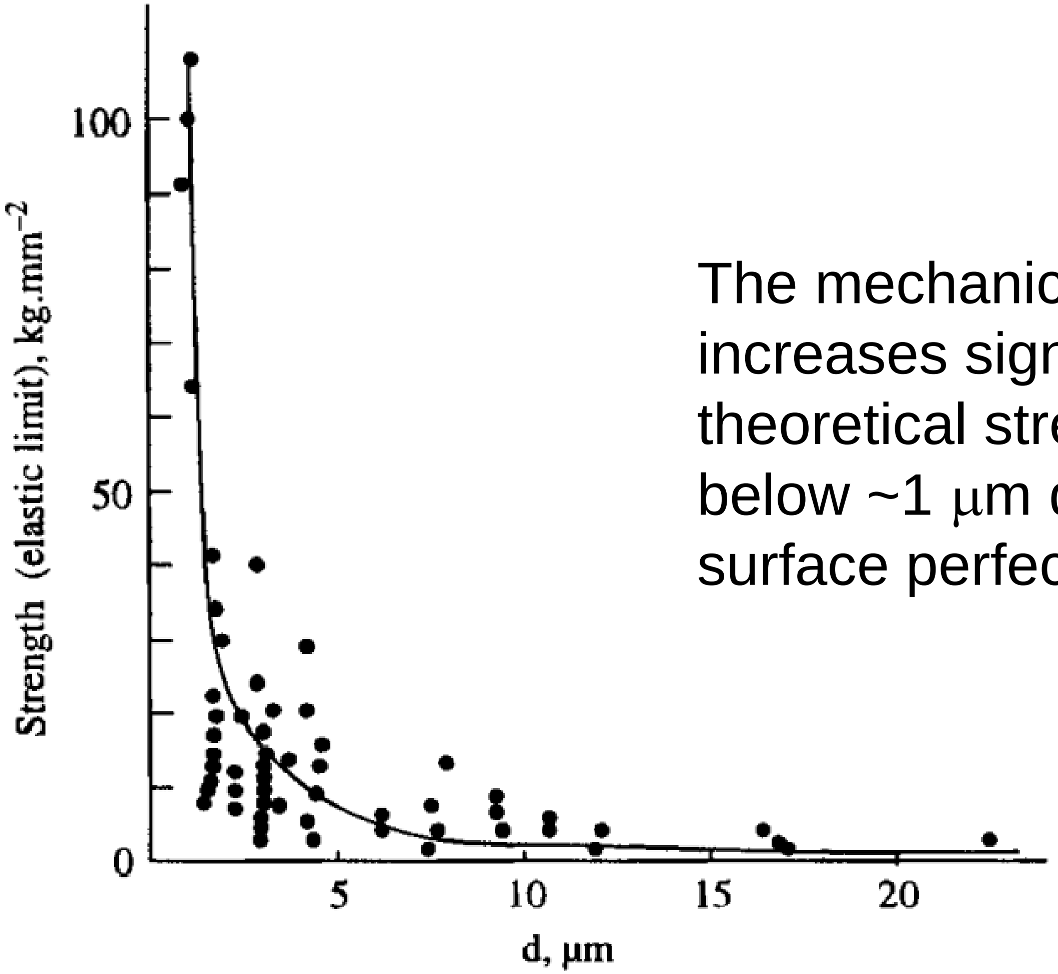
In general, smaller structures have less surface defects. It is particularly true when the materials are made through a bottom-up approach.

Vapor grown whiskers with diameters of 10 microns or less had no detectable steps on their surfaces by electron microscopy, whereas irregular growth steps were revealed on whiskers with diameters above 10 microns.

In the last few years, AFM and TEM have been applied for measuring the mechanical property of nanowires or nanorods.

Both AFM and TEM promise some direct evidence for the mechanical behavior of nanostructures and nanomaterials.

The Applied force per unit area before plastic deformation occurs



The mechanical strength of NaCl whiskers increases significantly and approaches the theoretical strength as the diameters decrease below ~1 μm due to an increased bulk and surface perfections

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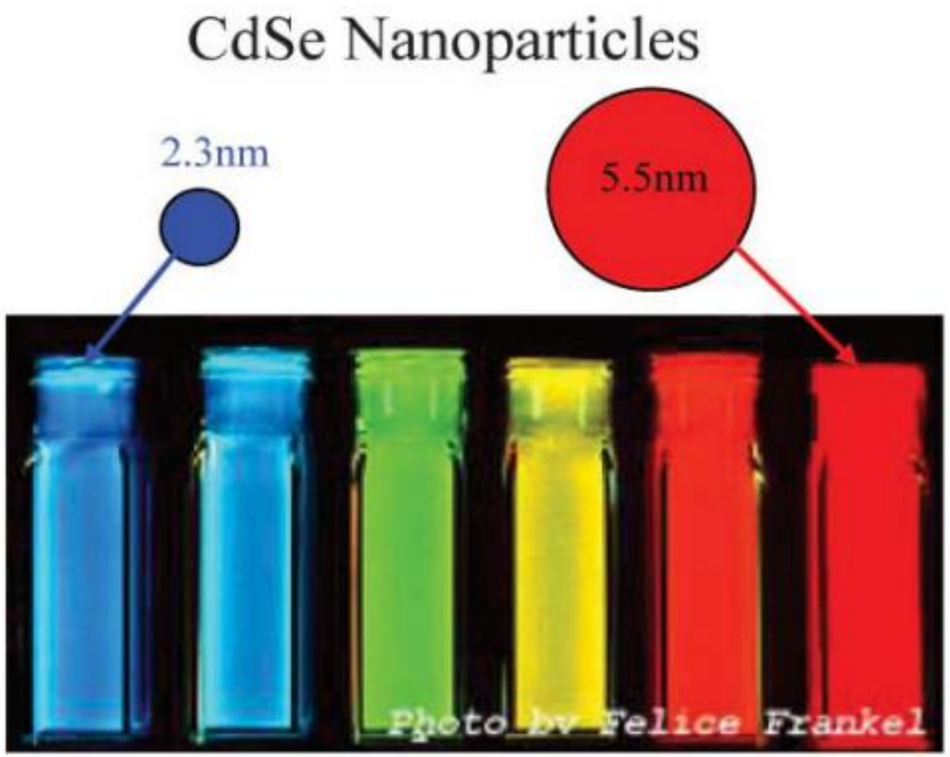
Lecture 05 dated 14th January 2025

Optical Properties of Nanomaterials

- **One of the most fascinating and useful aspects of nanomaterials**
- **Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis, photo-electrochemistry and biomedicine.**
- **The optical properties of nanomaterials depend on parameters like**
  - feature size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures.
- **Shape can have dramatic influence on optical properties of metal nanostructures.**



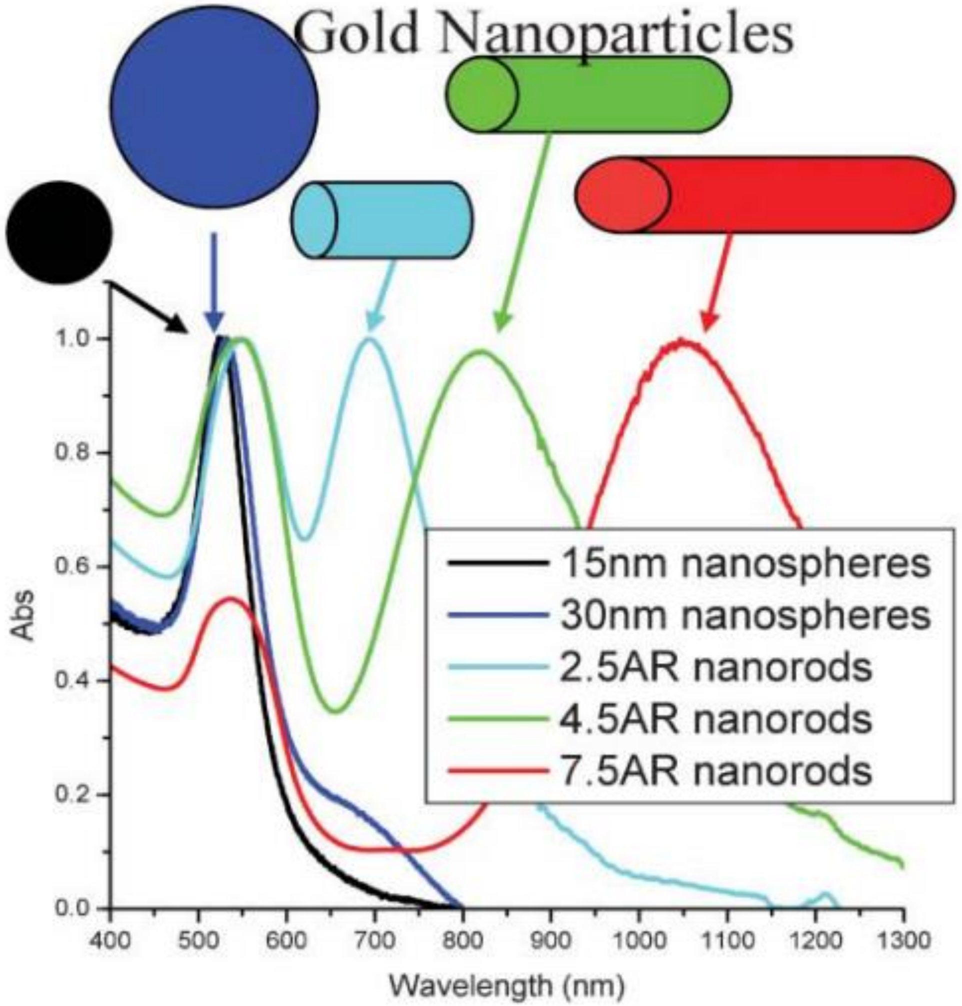


Fig.: Fluorescence emission of (CdSe) ZnS quantum dots of various sizes and absorption spectra of various sizes and shapes of gold nanoparticles (Chem. Soc. Rev., 2006, 35, 209–217).

The difference in the optical properties of metal & semiconductor nanoparticles

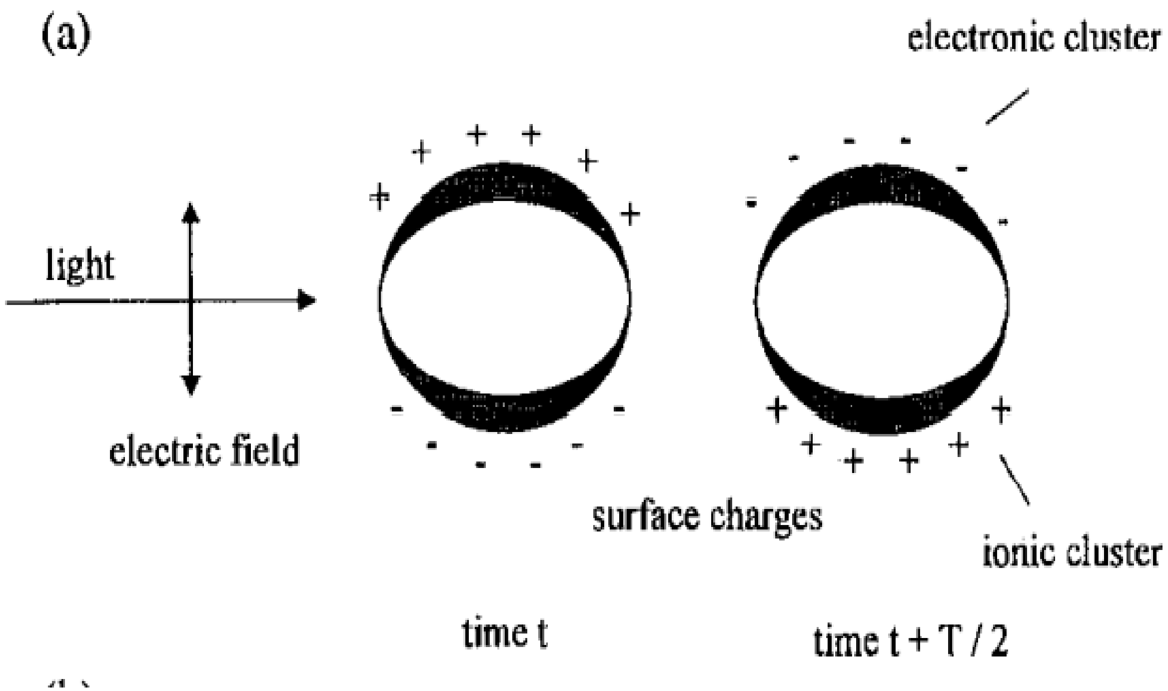
- With the CdSe semiconductor nanoparticles, a simple change in size alters the optical properties of the nanoparticles.
- When metal nanoparticles are enlarged, their optical properties change only slightly as observed for the different samples of gold nanospheres.
- However, when an anisotropy is added to the nanoparticle, such as growth of nanorods, the optical properties of the nanoparticles change dramatically.

1. Surface Plasmon Resonance

- Surface plasmon resonance is the coherent excitation of all the "free" electrons within the conduction band, leading to an in-phase oscillation
- When the size of a metal nanocrystal is smaller than the wavelength of incident radiation, a surface plasmon resonance is generated

Surface plasmon absorption of spherical nanoparticles & its size dependence

- The electric field of an incoming light wave induces a polarization of the (free) conduction electrons with respect to the much heavier ionic core of a spherical metal nanoparticle.
- A net charge difference is only felt at the nanoparticle surfaces, which in turn acts as a restoring force.
- In this way a dipolar oscillation of the electrons is created with period T.
- SPR is a dipolar excitation of entire particle between the negatively charged free electrons and its positively charged lattice

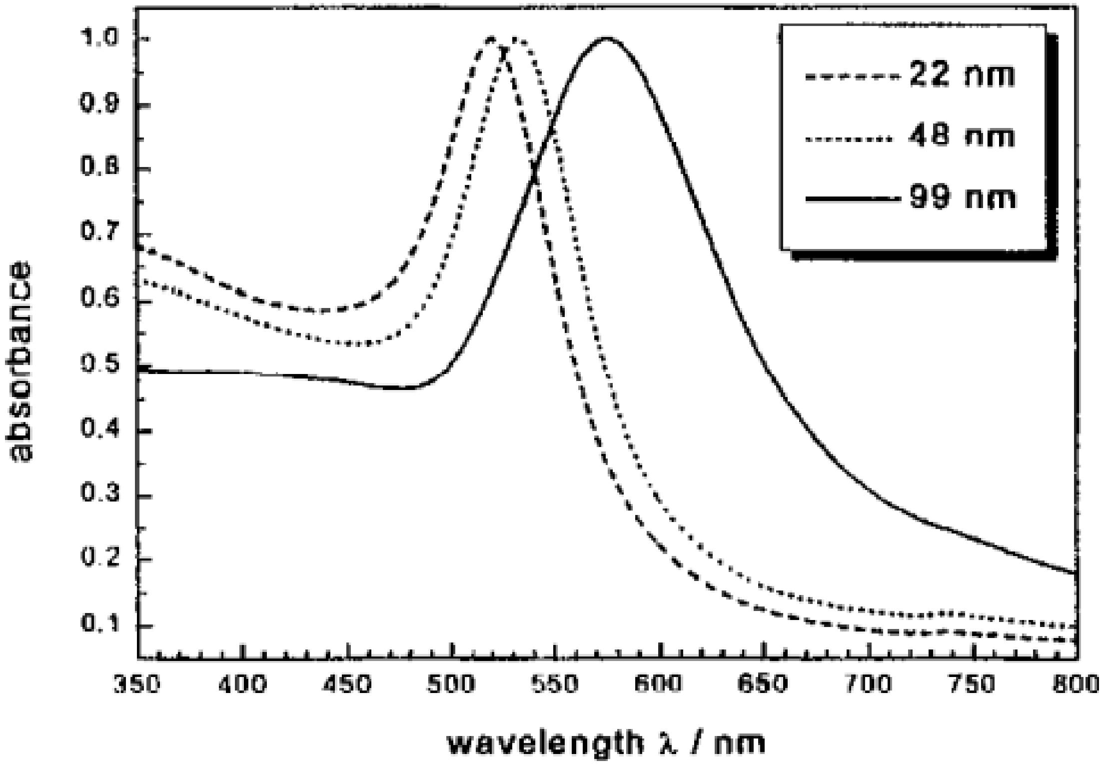


A schematic illustrating the excitation of the dipole surface plasmon oscillation.

Surface plasmon absorption of spherical nanoparticles & its size dependence

- Optical absorption spectra of 22, 48 & 99nm spherical **gold nanoparticles**.
- The broad absorption band corresponds to the surface plasmon resonance.
- The energy of the surface plasmon resonance depends on both the free electron density & the dielectric medium surrounding the nanoparticle
- For larger nanoparticle, the resonance sharpens as the scattering length increases.
- Noble metals have the resonance frequency in the visible light range.

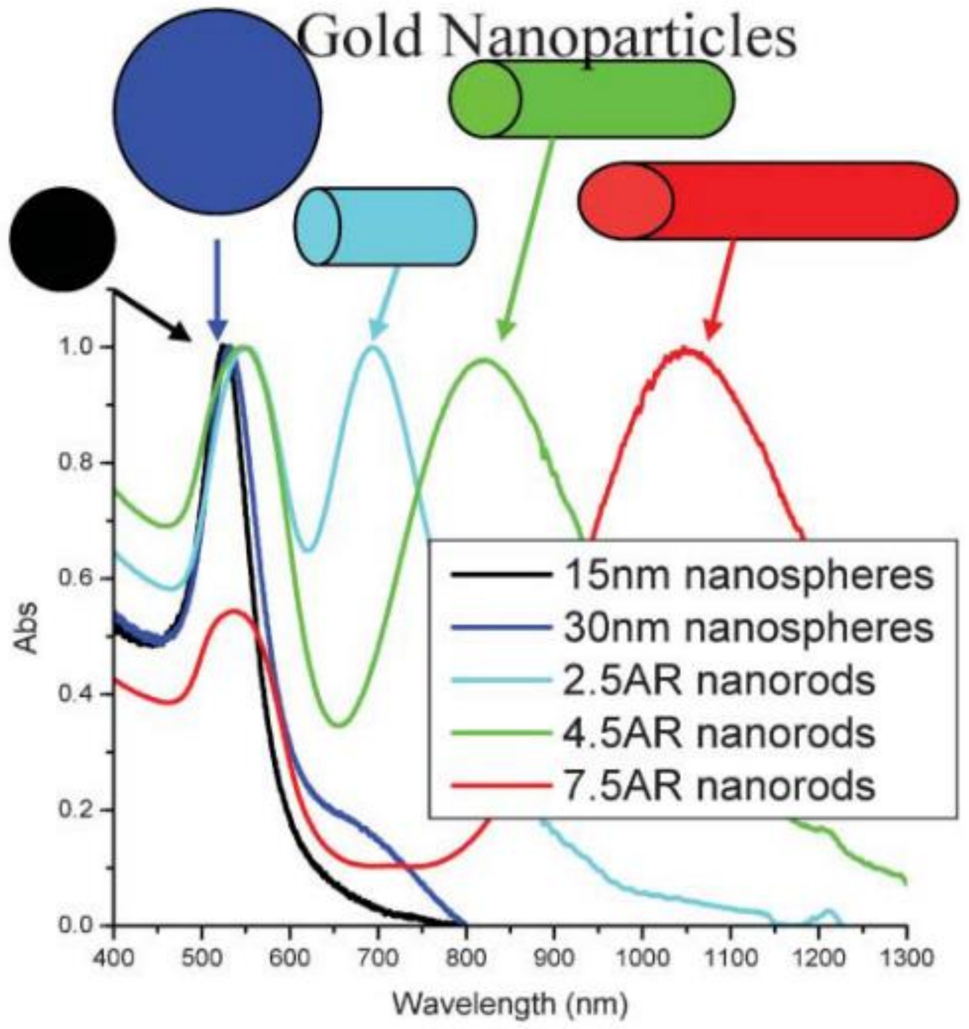
(b)



Ref.: S. Link and M.A. El-Sayed Int. Rev. Phys. Chem. 19,409 (2000).

Metal nanowires surface plasmon resonance

- Similar to nanoparticles, metal nanowires have surface plasmon resonance properties
- Metal nanorods exhibited **two surface** plasmon resonance **modes**, corresponding to the transverse & longitudinal excitations.
- The wavelength of **transverse mode** is fixed around 520 nm for Au and 410 nm for Ag
- The **longitudinal modes** can be easily tuned to span across the spectral region from visible to near infrared by controlling their aspect ratios
- It is demonstrated that gold nanorods with an aspect ratio of 2 - 5.4 could fluoresce with a quantum yield more than one million times that of the bulk metal



Electrical properties of Nanoparticles

- The effects of size on electrical conductivity of nanostructures and nanomaterials are complex, and they are based on distinct mechanisms.
- These mechanisms can be generally grouped into four categories:
  - surface scattering including grain boundary scattering,
  - quantized conduction including ballistic conduction, Coulomb charging and tunneling,
  - widening and discrete of band gap, and
  - change of microstructures.
- In addition, **increased perfection**, such as reduced impurity, structural defects and dislocations, would affect the electrical conductivity of nanostructures and nanomaterials.

Nano Sensors

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Lecture 06 dated 16th January 2025

1. Surface scattering

- Electrical conduction in metals or Ohmic conduction is described by the various electron scattering, and
- the total resistivity, ρ_T, of a metal is a combination of individual and independent scattering, known as Matthiessen's rule:

$$\rho_T = \rho_{Th} + \rho_D$$

ρ_{Th} is the thermal resistivity and ρ_D the defect resistivity.

- Electron collisions with vibrating atoms (phonons) displaced from their equilibrium lattice positions are the source of the thermal or phonon contribution, which **increases linearly** with **temperature**.
- Impurity atoms, defects such as vacancies, and grain boundaries locally **disrupt the periodic electric potential** of the lattice & cause electron scattering, which is **temperature independent**.

- The **defect resistivity** can be further divided into impurity resistivity, lattice defect resistivity, and grain boundary resistivity.
- Considering individual electrical resistivity **directly proportional** to the respective mean free path (λ) between collisions, the Matthiessen's rule can be written as:

$$1/\lambda_T = 1/\lambda_{Th} + 1/\lambda_D$$

- As per theory that λ_T ranges from several tens to hundreds of nanometers
- **Reduction** in material's dimensions would have **two** different effects on electrical resistivity:
- **One** is an increase in crystal perfection or reduction of defects, which result in a reduction in defect scattering and thus **reduction in resistivity**.
- The defect scattering makes a minor contribution to the total electrical resistivity of metals at room temperature, thus the reduction of defects has a very small influence on the electrical resistivity, **mostly unnoticed** experimentally.

- The **other** is to create an additional contribution to the total resistivity due to **surface scattering**, which plays a very important role in the **total electrical** resistivity of nanosized materials.
- If the mean free electron path, λ_S, due to the surface scattering is the **smallest**, then it will dominate the total electrical resistivity:

$$\mathbf{1/\lambda_T = 1/\lambda_{Th} + 1/\lambda_D + 1/\lambda_S}$$

- In nanowires and thin films, the surface scattering of electrons results in **reduction** of electrical **conductivity**.
- When the critical dimension of thin films & nanowires is **smaller** than the electron mean-free path, the motion of electrons will be interrupted through collision with the surface.
- The electrons undergo either elastic or inelastic scattering.

Elastic vs Inelastic scattering

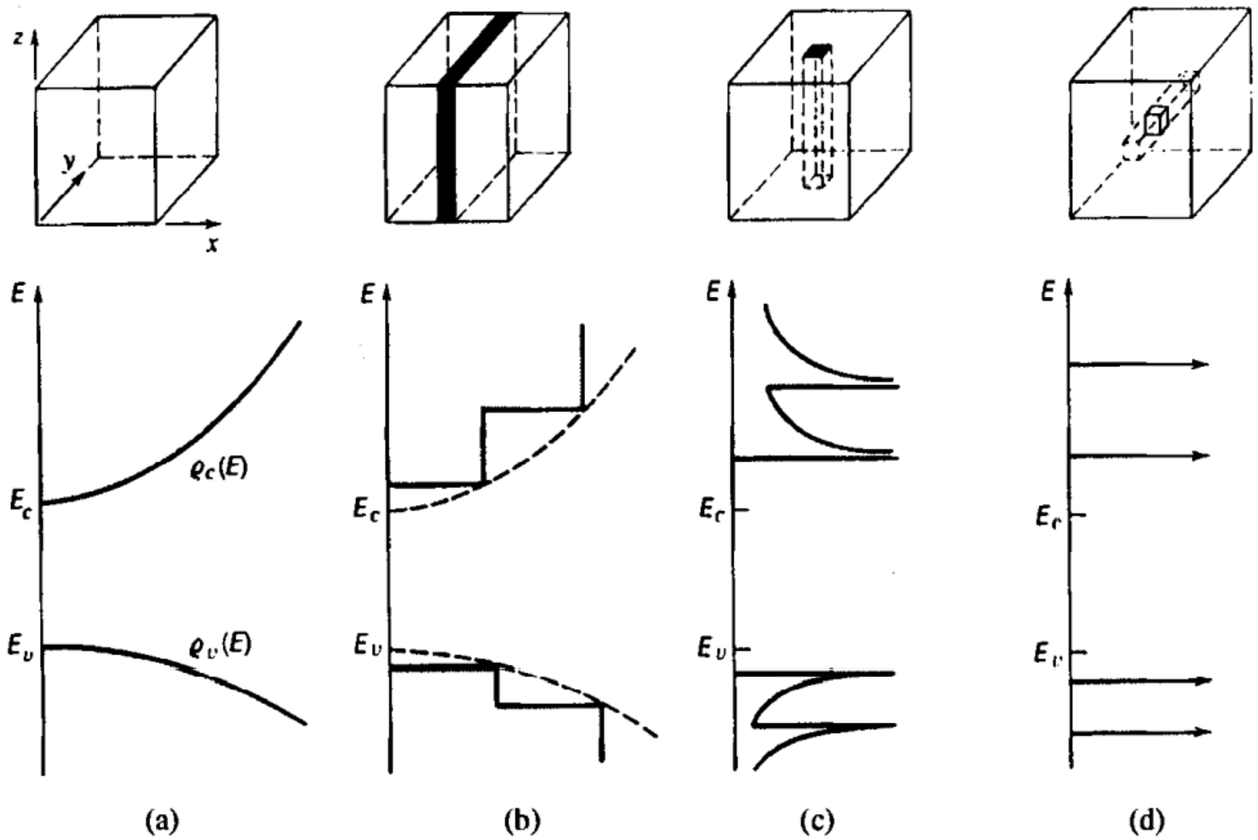
- In **elastic**, also known as specular scattering, the **electron reflects** in the same way as a photon reflects from a mirror.
- In this case, the electron **does not lose** its energy & its **momentum** or **velocity** along the direction parallel to the surface is preserved.
- Hence, the electrical conductivity remains the **same** as in the bulk & there is **no size effect** on the conductivity.
- When scattering is **totally inelastic**, or non-specular or diffuse, the electron mean free path is terminated by impinging on the surface.
- After the collision, the electron trajectory is independent of the impingement direction and the subsequent **scattering angle is random**
- Consequently, the **scattered electron loses its velocity** along the direction parallel to the surface or the conduction direction, & the **electrical conductivity decreases**.
- There will be **a size effect on electrical conduction**.

- The surface inelastic scattering of electrons & phonons would result in a **reduced thermal** conductivity of nanostructures and nanomaterials, similar to the surface inelastic scattering on electrical conductivity

- Theoretical studies suggest that thermal conductivity of **silicon nanowires** with a diameter less than 20nm would be significantly smaller than the bulk value.

2. Change of electronic structure

- A reduction in characteristic dimension **below** a critical size, i.e. the electron de Broglie wavelength, results in a **change of electronic structure**, leading to widening and discrete band gap.
- Such a change may result in a **reduced electrical conductivity**.
- As their diameters are reduced below certain values, some **metal** nanowires may undergo a transition to become **semiconducting**, and
- semiconductor nanowires may become insulators.



Discrete electronic configurations in nanocrystals, nanowires & thin films

- Such a change can be partially attributed to the **quantum** size effects, i.e. increased electronic energy levels when the dimensions of materials are below a certain size
- E.g.,
  - single crystalline Bi nanowires undergo a metal-to-semiconductor transition at a diameter of ~52 nm and
  - the electrical resistance of Bi nanowires of ~40nm was reported to decrease with decreasing temperature.
  - GaN nanowires of 17.6 nm in diameter was found to be still semiconducting,
  - Si nanowires of ~15 nm became insulating

Electrical properties of Nanoparticles

1. Surface scattering
2. Change of electronic structure
3. Quantum transport
4. Effect of microstructure

Nano Sensors

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Lecture 07 dated 21st January 2025

3. Quantum transport

- Quantum transport in small devices and materials has been studied extensively covering a brief on ballistic conduction, Coulomb charging and tunneling conduction.

Ballistic conduction:

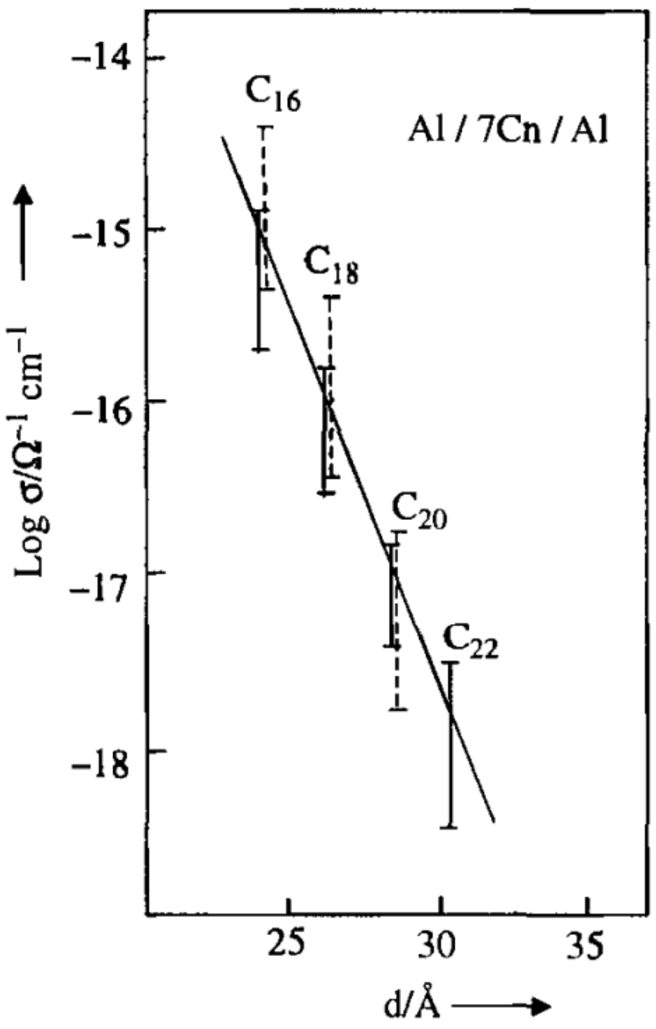
- It occurs when the length of conductor is smaller than the electron mean-free path.
- In this case, each transverse waveguide mode or conducting channel contributes to the total conductance.
- In ballistic transport, **no energy is dissipated** in the conduction, and
- there exist **no elastic scattering**
- When elastic scattering occurs, the transmission coefficients, and thus the electrical conductance will be reduced, which is then no longer precisely quantized.

Coulomb blockade or Coulomb charging:

- It occurs when the contact resistance is larger than the resistance of nanostructures in question and
- when the total capacitance of the object is so small that adding a single electron requires significant charging energy.
- Metal or semiconductor nanocrystals of a few nanometers in diameter exhibit quantum effects that give rise to discrete charging of the metal particles.
- Such a discrete electronic configuration permits one to pick up the electric charge one electron at a time, at specific voltage values.
- This **Coulomb blockade behavior**, also known as "Coulombic staircase", has originated the proposal that nanoparticles with diameters below 2-3 nm may become basic components of single electron transistors (SETs).
- **To add a single charge** to a **semiconductor** or **metal** nanoparticle requires **energy**, since electrons can no longer be dissolved into an effectively infinite bulk material.

Tunneling conduction

- It is another charge transport mechanism important in the nanometer range.
- Tunneling involves charge transport through an insulating medium separating two conductors that are extremely closely spaced.
- It is because the electron wave functions from two conductors overlap inside the insulating material, when its thickness is extremely thin.
- The tunneling conductivity as a function of C_{14} to C_{23} fatty acid monolayers is demonstrated; the electrical conductivity decreases exponentially with increasing thickness of insulating layer.
- Under such conditions, electrons are able to tunnel through the dielectric material when an electric field is applied.



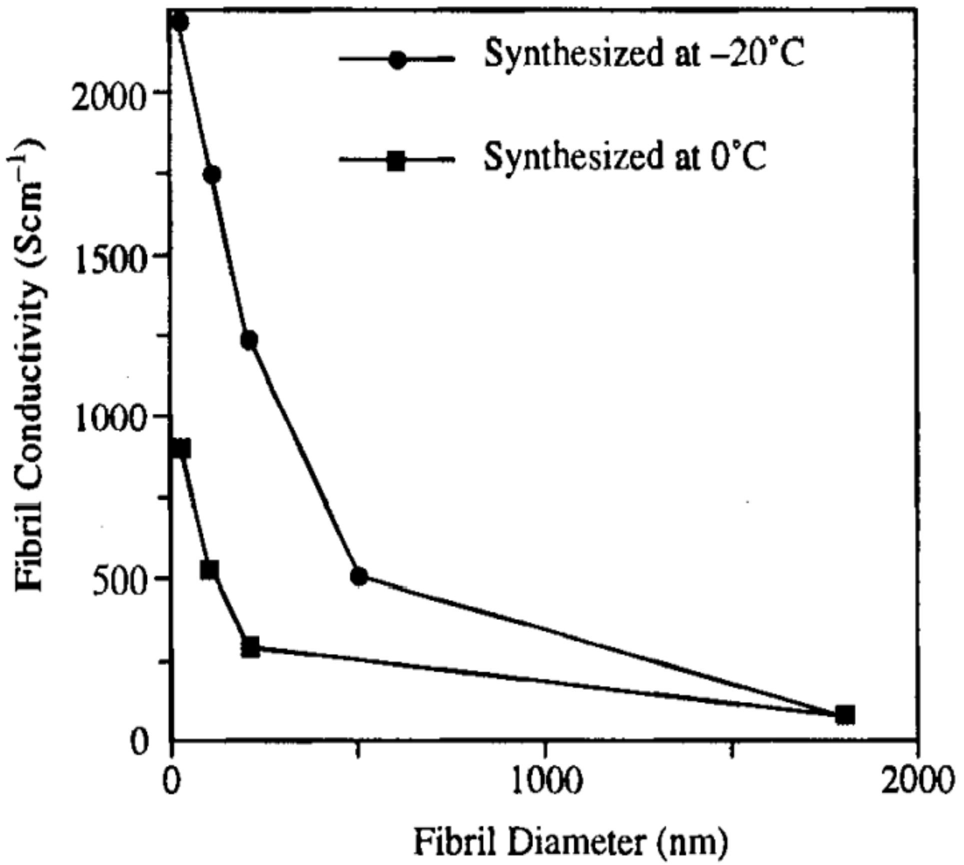
Note:

1. Coulomb charging and tunneling conduction are not material properties.

2. They are system properties, and dependent on the characteristic dimension.

4. Effect of microstructure

- Electrical conductivity may change due to the ordered microstructure, as the size is reduced to a nanometer scale.
- E.g., polymer fibers have demonstrated an enhanced electrical conductivity.
- The enhancement was explained by the ordered arrangement of the polymer chains.
- Within nanometer fibrils, polymers are aligned parallel to the axis of the fibrils, which results in
  - **increased** contribution of **intramolecular** conduction and
  - **reduced** contribution of **intermolecular** conduction



The electrical conductivity of poly-heterocyclic fibrils as a function of diameter

Nano bioelectronics

- **Nano-bioelectronics** represents an interdisciplinary field that combines nanomaterials with biology and electronics
  - It has potential to overcome existing challenges in bioelectronics

- **Bioelectronics** can be defined as the merger of electronics with biological systems, where

  - a bioelectronic device transduces signals from the biological system to electrical signals at the bio-electronics interface.

- The development of bioelectronics has resulted in vital biomedical devices, like blood glucose sensors, cardiac pacemakers, deep-brain stimulators, etc.

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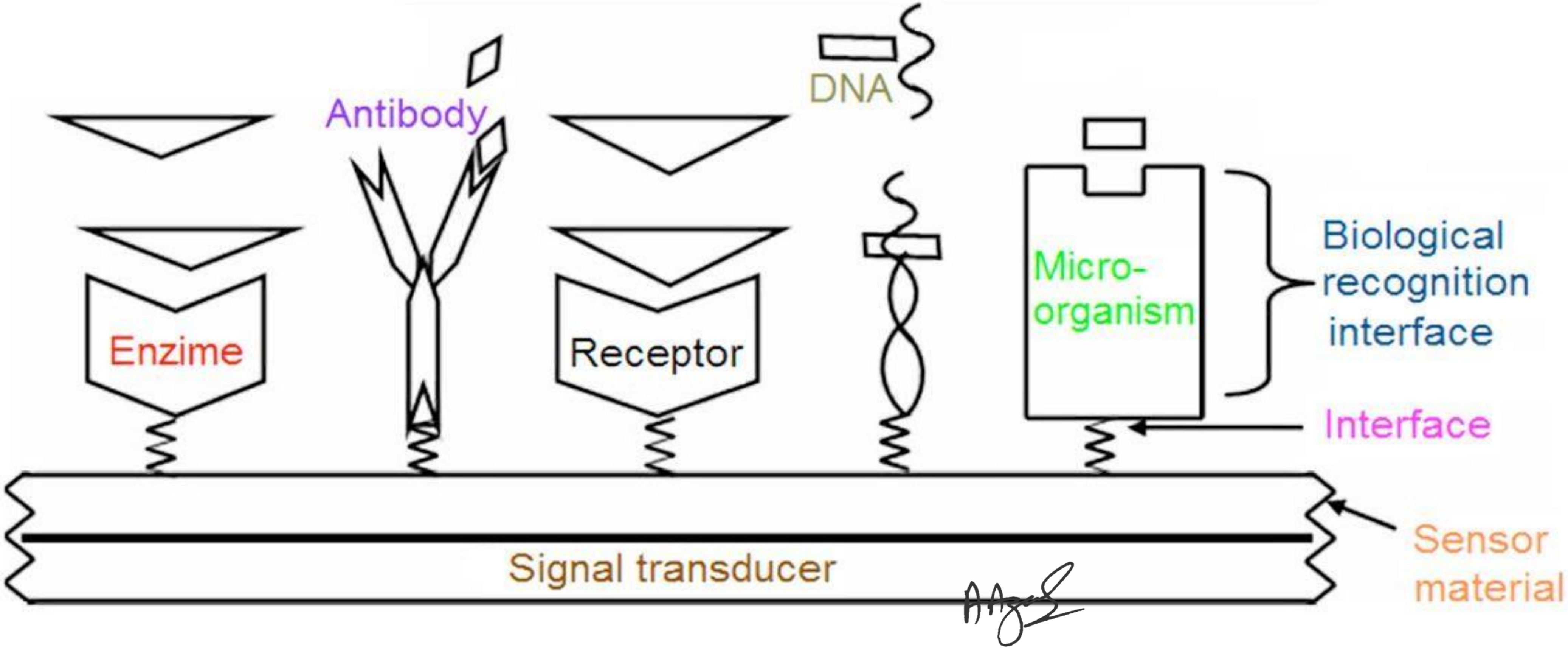
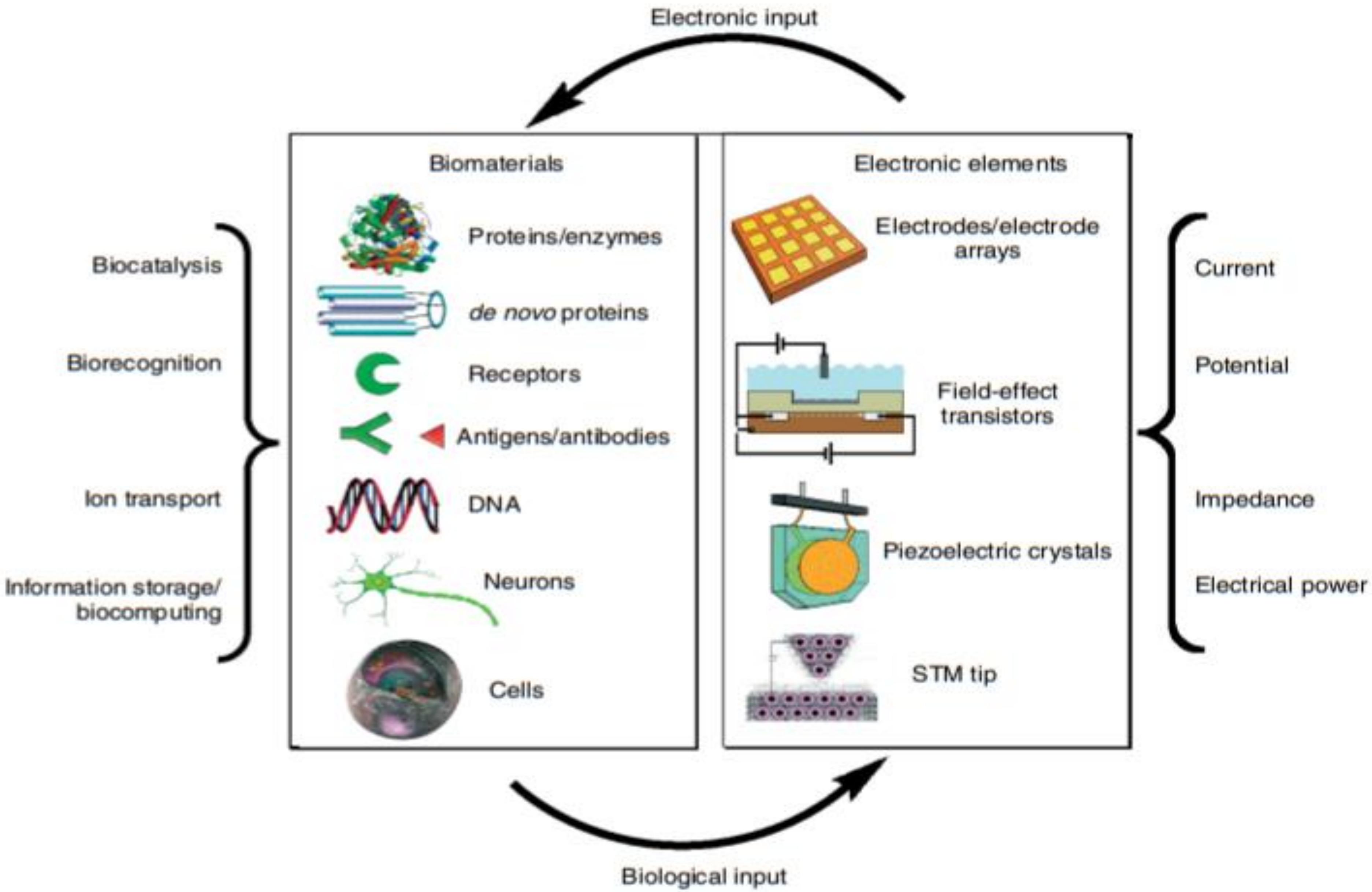
Lecture 08 dated 23rd January 2025

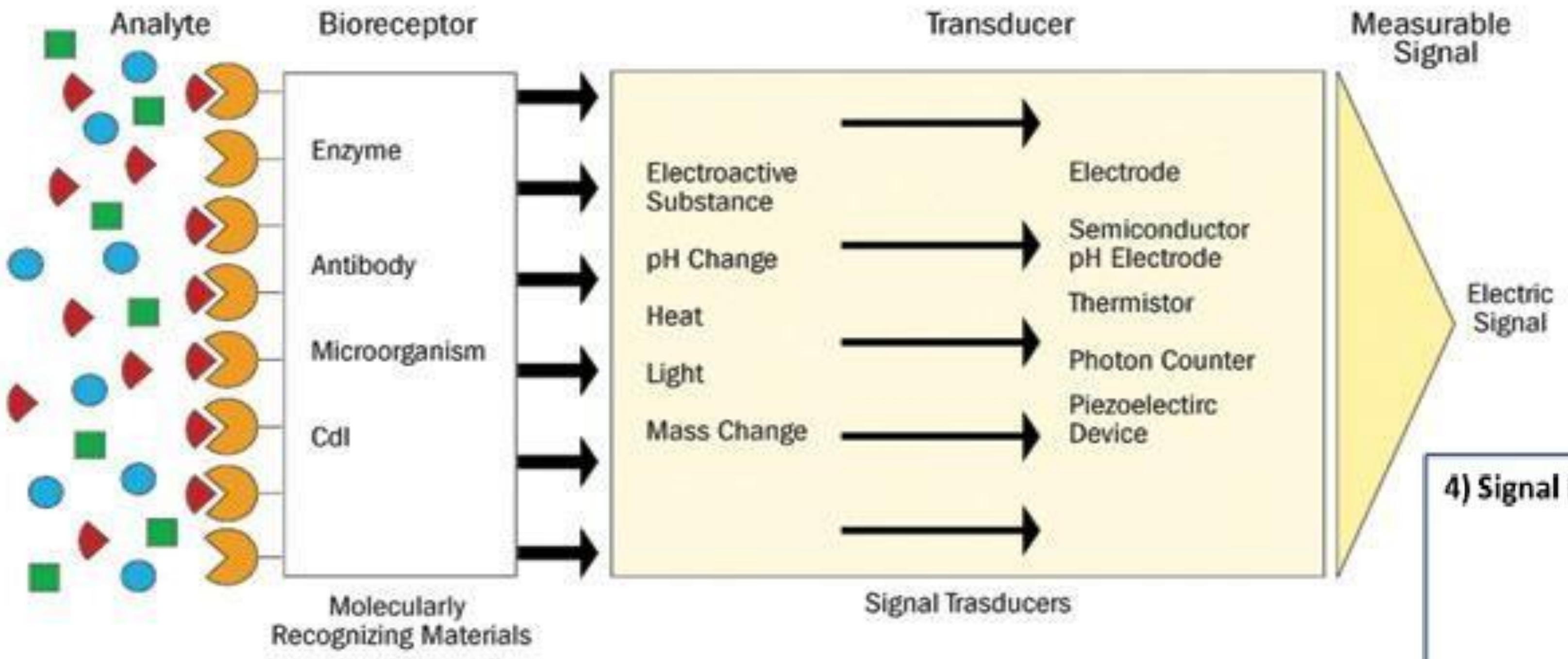
Schematic representation of nano-biosensor components



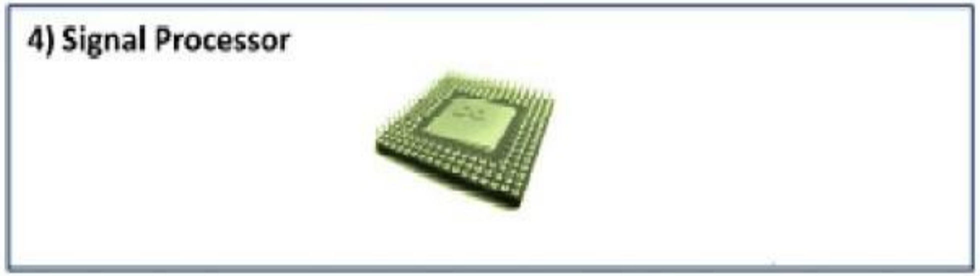


Integrated systems of biomaterials and electronic elements for bioelectronic application

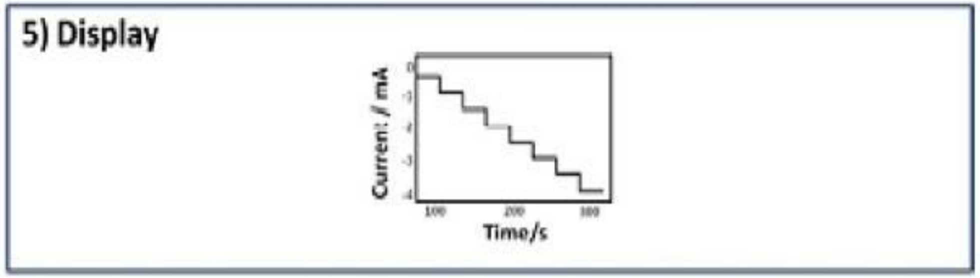
Biosensor



Analyte
Bioreceptor
Transducer
Measurable Signal
Enzyme
Antibody
Microorganism
CdI
Electroactive Substance
pH Change
Heat
Light
Mass Change
Electrode
Semiconductor pH Electrode
Thermistor
Photon Counter
Piezoelectirc Device
Electric Signal
Molecularly Recognizing Materials
Signal Trasducers

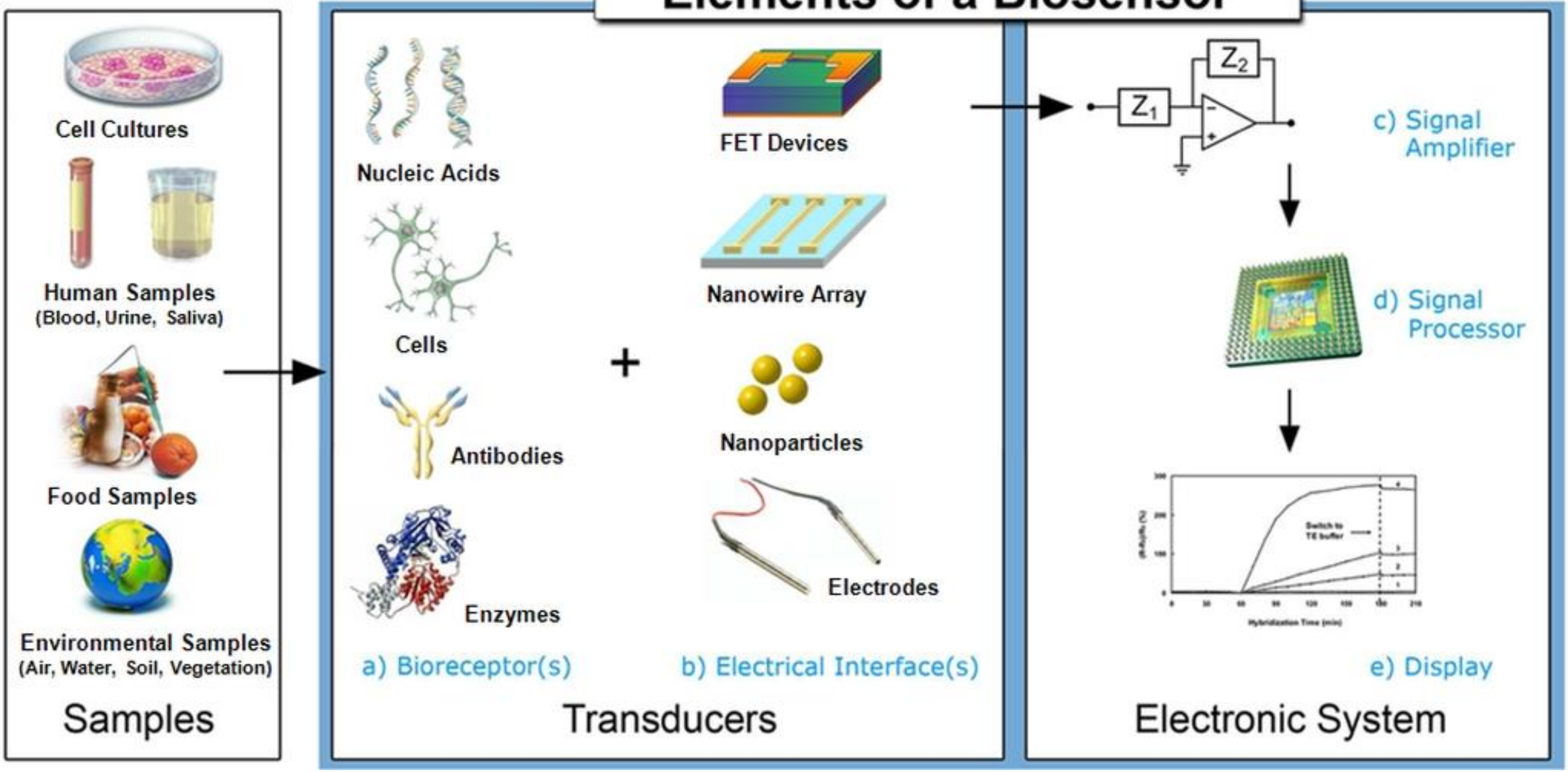


4) Signal Processor



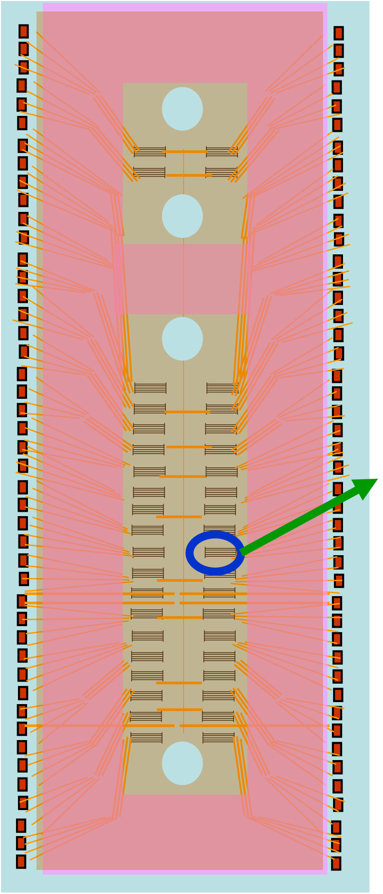
5) Display
Current / mA
Time/s

Elements of a Biosensor

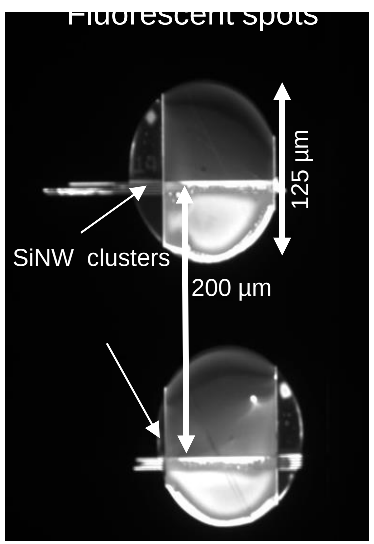


Integrated Detection Module

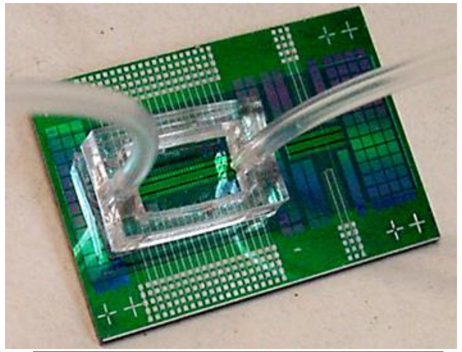
NW Array Chip



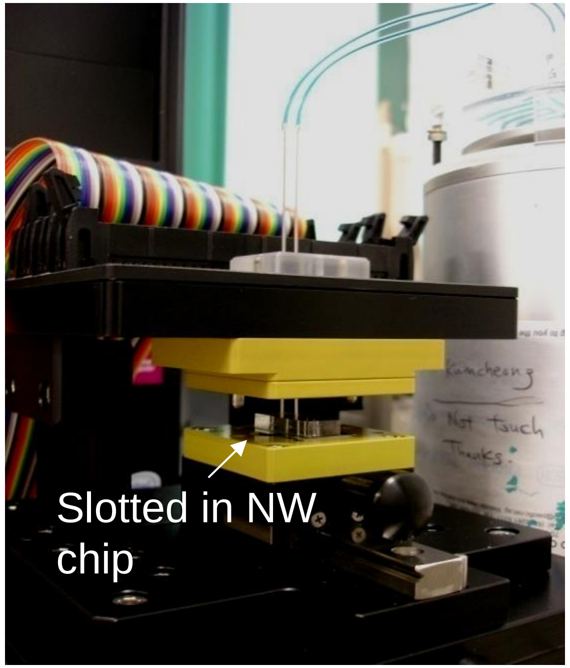
36 clusters of NW



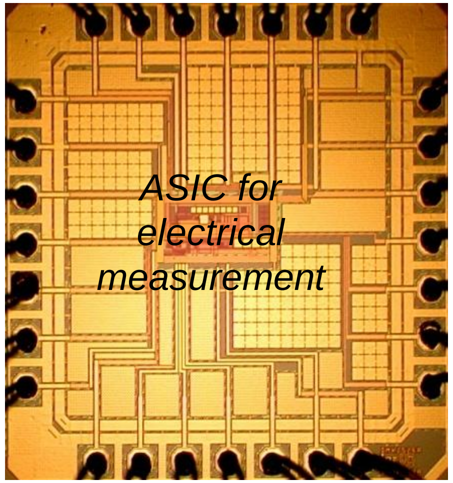
Spotting of capture probes *using an array spotter*



SiNW chip with fluid exchange



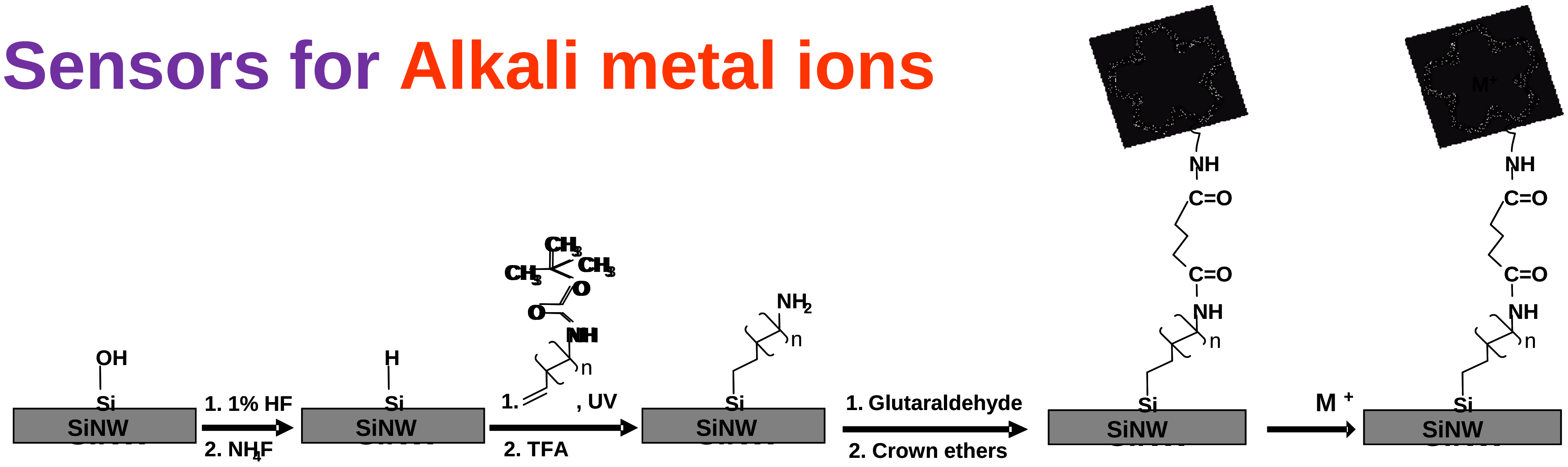
Mini-electrical measurement station

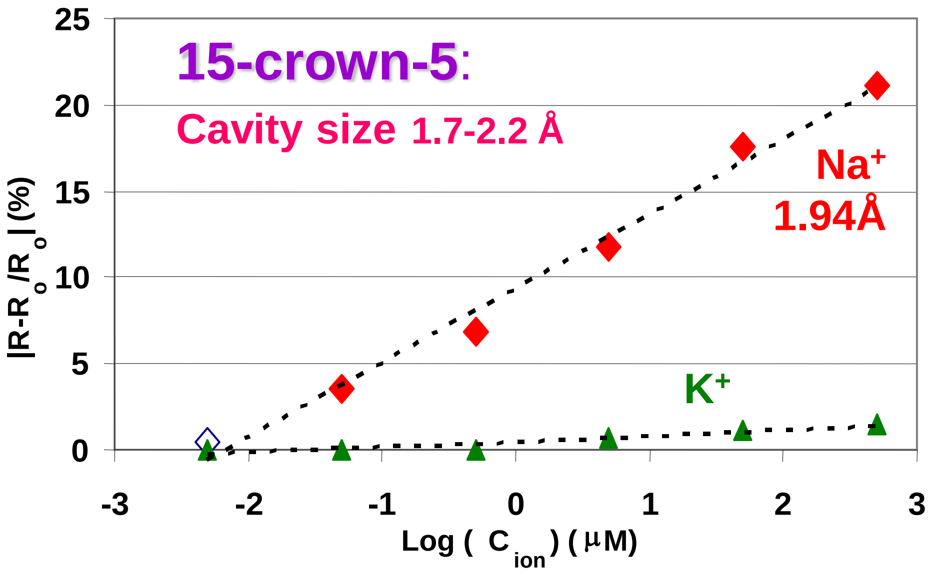


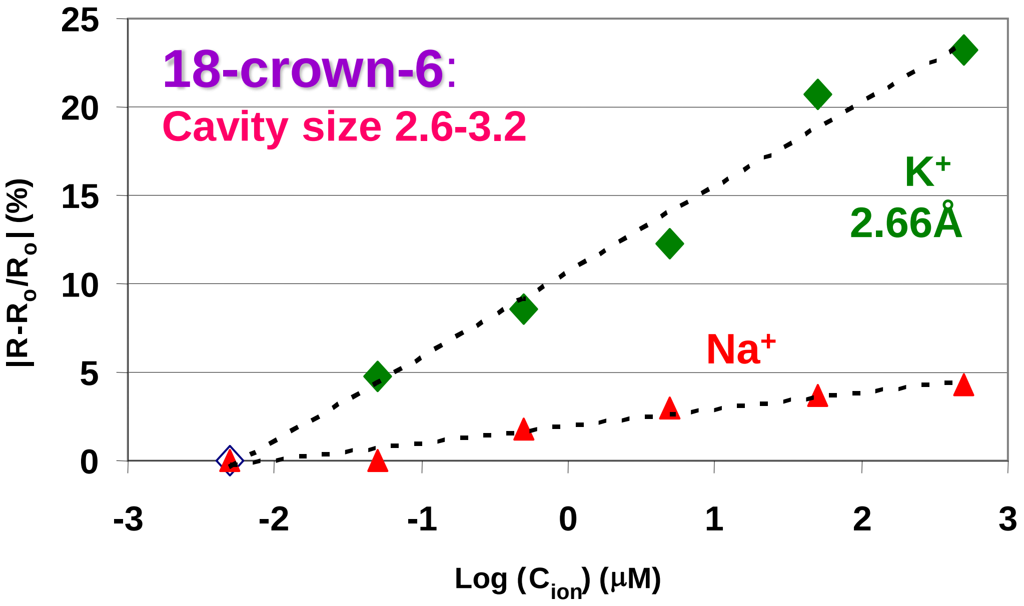
Peripheral electronics

Display / Storage of data

Sensors for Alkali metal ions



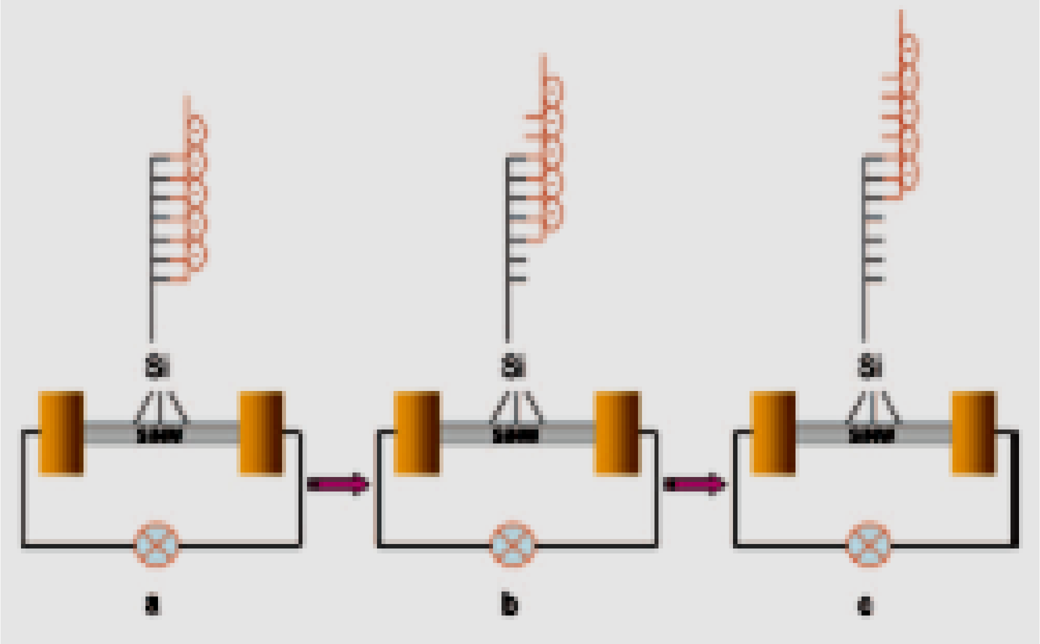


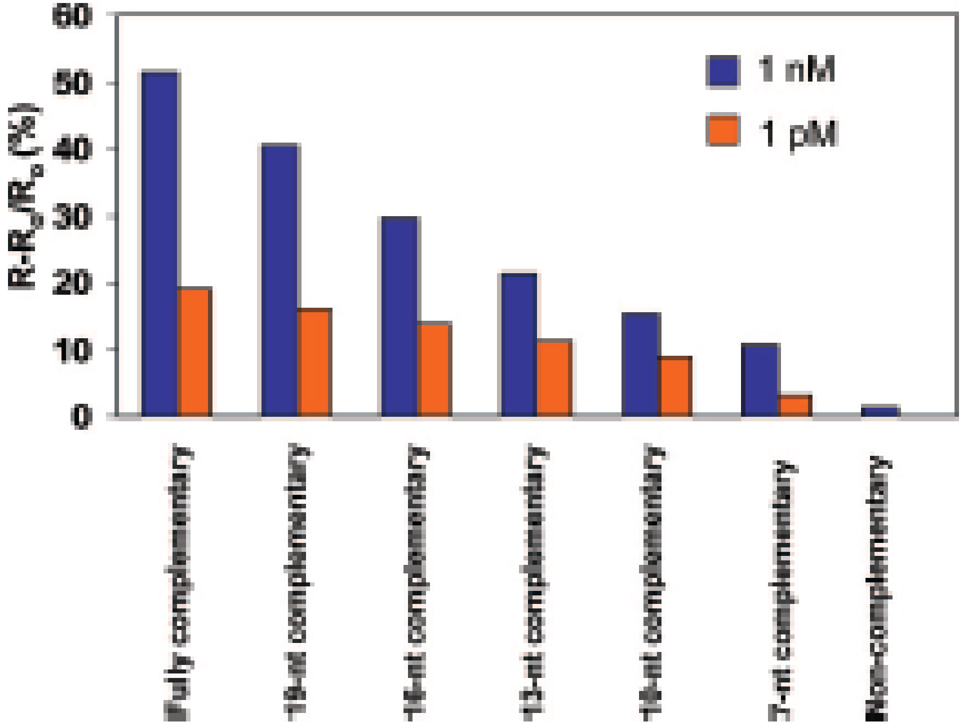


Detection limit of 50 nM; lower by 3 orders than conventional crown ether–based ion-selective electrodes.

G. Zhang, **Ajay Agarwal**, et al., **Appl. Phy. Lett.** 90, 2007, pp. 233903

DNA Sensing by SiNW:





Variation of field effect of the SiNW Sensor caused by varying hybridization sites of Target DNA to PNA

Distinguishable resistance change of the SiNW caused by varying hybridization sites at two different concentrations of the target DNAs.

G. Zhang, **Ajay Agarwal**, et al., **Nano Letter**, 8, (2008) 1066.

Questions ??