Semiconductor Heterojunctions in Photocatalytic and Photosynthetic Processes: Genesis, Misconceptions, Pitfalls and Best Practises

HARIPRASAD NARAYANAN

National Centre for Catalysis Research

November 25, 2018 ; 9.30 am
M V C Sasthri Hall

Intentions of the Presentation

1. Revisit the current status of semiconductor heterojunction in photocatalytic and photosynthetic processes
2. Why this revisit?
3. Special Issue "Heterojunction-Based Photocatalysts and Photoelectrodes for Water Splitting and CO_2 Reduction: From Fundamentals to Applications"
4. Semiconductor Heterojunctions in Photocatalytic and Photosynthetic Processes: Genesis, Misconceptions, Pitfalls and Best Practises
5. Hope this will initiate some discussion within the research community.

Genesis

- The interface between two dissimilar materials
- Junction between two monocrystalline semiconductor material
- Detailed history should be addresses.
- A.I. Gubavanov theoretically analysed heterojunction combinations in 1951.
- H. Kroemer in 1957 suggested the possibility of anisotropic heterojunctions. (Nobel Prize in 2000)
- First isotype and anisotype heterojunction fabricated by R.L Anderson (Syracuse University) in 1960.
- Anderson rule
- Nozik in 1977 applied this concept to photoelectrodes and patented it.
- In 1984, Nick serpone group made a heterojunction (isotype) of TiO_2/CdS and reffered it as Inter-particle Electron Transfer (IPET)

Genesis

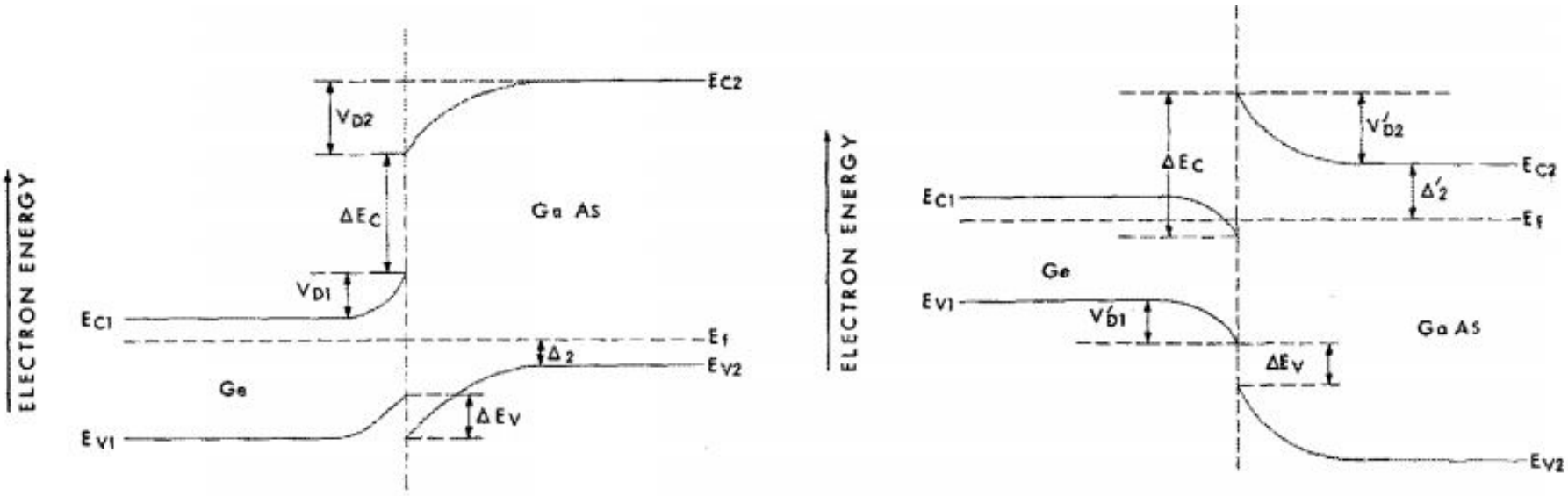


Figure: Energy band diagram for n-p and n-n heterojunctions at equilibrium; Anderson in 1960

- Anderson's rule ignores the real chemical bonding effects that occur with a small or nonexistent vacuum separation: interface states which may have a very large electrical polarization and defect states, dislocations and other perturbations caused by imperfect crystal lattice matches.

Genesis

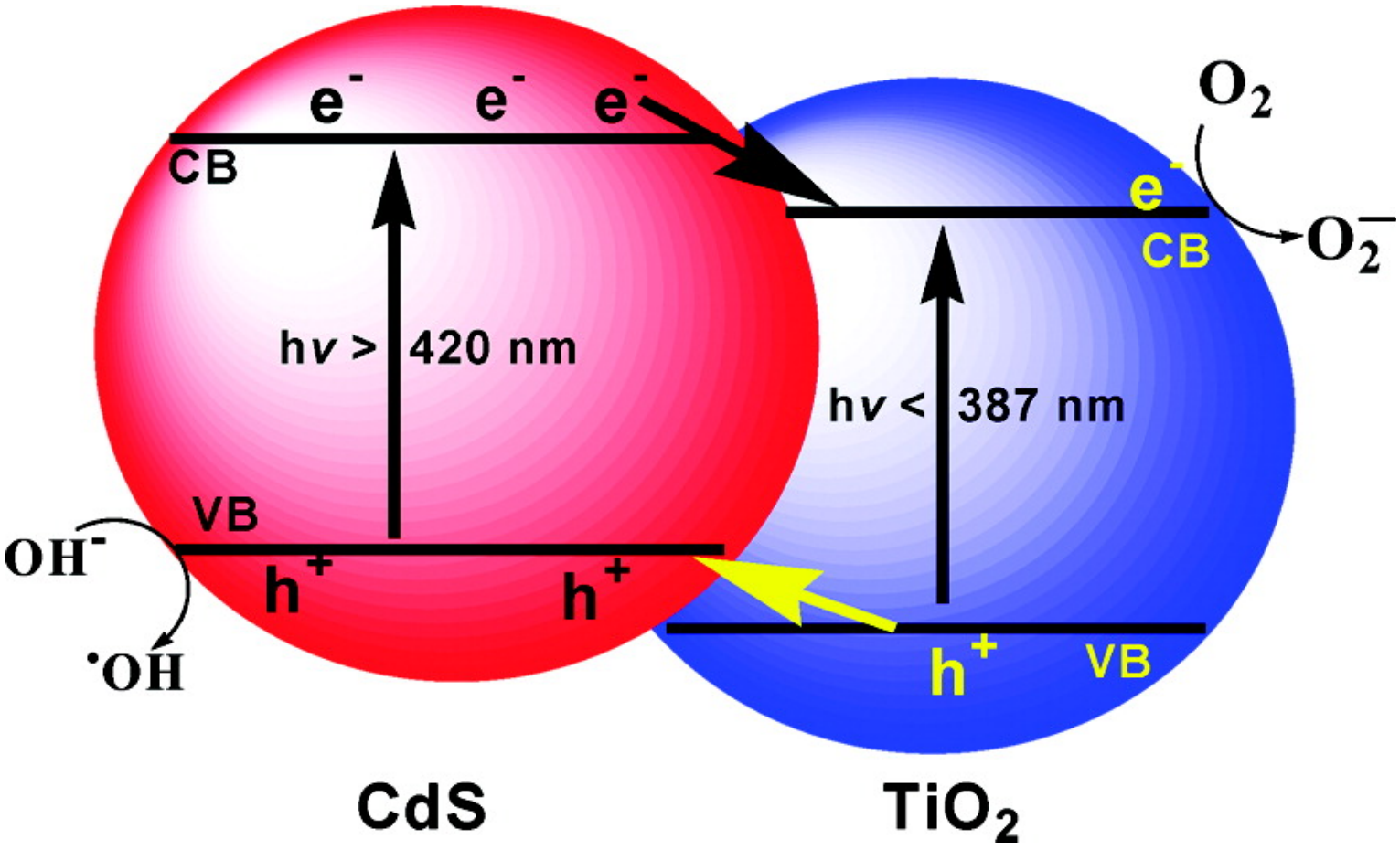


Figure: IPET process from the conduction band (CB) of photoexcited CdS to the CB of TiO_2. Hole transfer occurs from the valence band (VB) of TiO_2 to the VB of CdS. This leads to significant charge separation and to more efficient chemistry at the surface of the coupled particles.

Structure of Heterojunction Interface

- An in-depth investigation of literature is required.
- Abrupt Anisotype Hetrojunction
  1. Diffusion Model
  2. Emission Model
  3. Emission-Recombination Model
  4. Tunneling-Recombination Model
- Abrupt Isotype Heterojunction
  1. Emission Model
  2. Diffusion Model
  3. Double-Schottky-diode Model
  4. Tunnelling Model

Heterojunctions at Equilibrium

- Critical points in determining the electronic properties of a semiconductor heterojunction, assuming structurally and chemically perfect materials, are the **energy gaps**, **electron affinities**, and **doping types and levels**.
- The energy gaps and electron affinities of flat band semiconductor heterojunctions lead to three possible band-edge configurations
  1. "**Straddling**" is the situation where the conduction and valence band edges of the narrow-gap semiconductor lie within the energy gap of the widegap semiconductor.
  2. "**Offset**" refers to a situation where the energy gaps are roughly equal but the electron affinities are different. Further, that the difference is less than the energy gap of either constituent.
  3. "**Broken gap**" semiconductor heterojunctions are composed of semiconductors with such extreme differences in electron affinity that the band gaps do not overlap at all.
- Issue in these junctions is the energy of the two band edges.

The Rules of Thumb

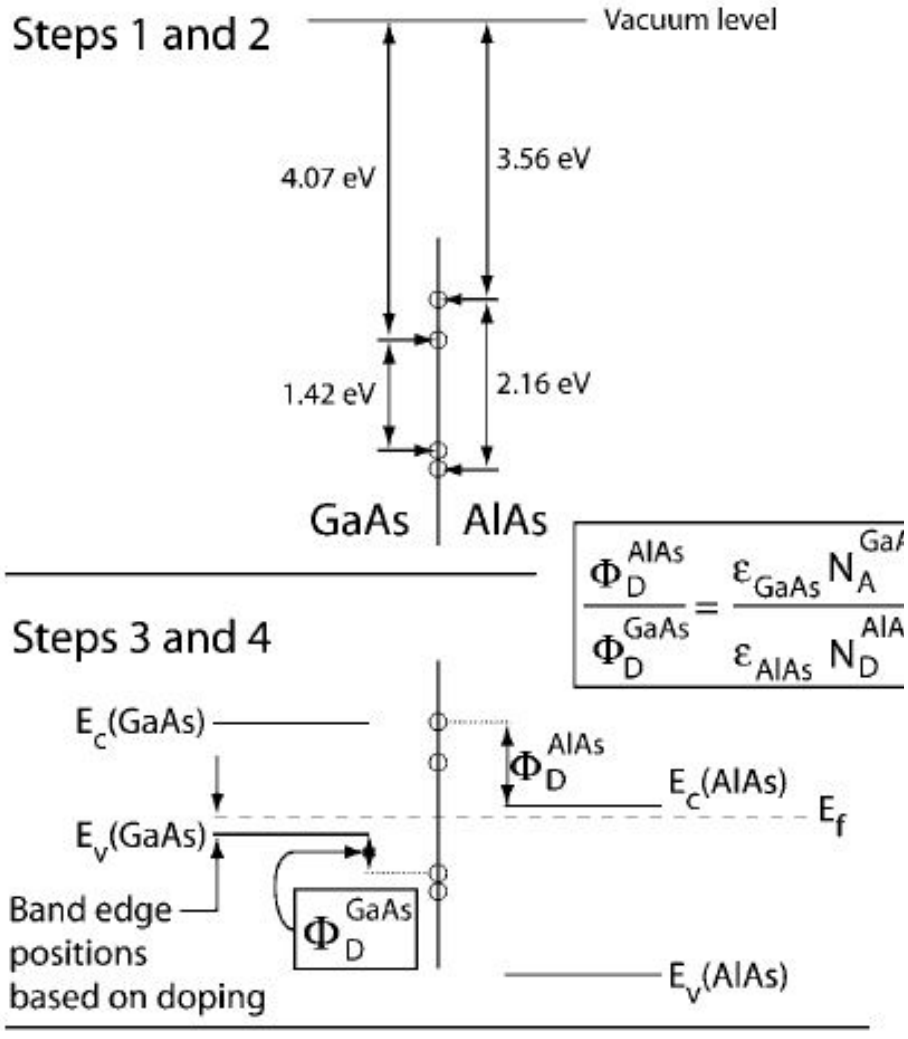
- There are some simple "rules of thumb" which indicate the trends one can expect in band edges as a function of which elements are changed across the junction.
  1. Linearity and Transitivity

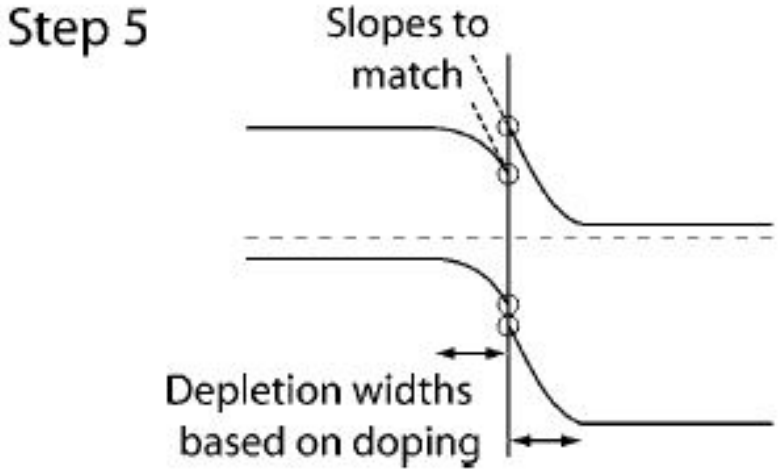
$$\Delta E_V(A:B) = \Delta E_V(B) - \Delta E_V(A)$$

$$\Delta E_V(A:B) + \Delta E_V(B:C) + \Delta E_V(C:A) = 0$$

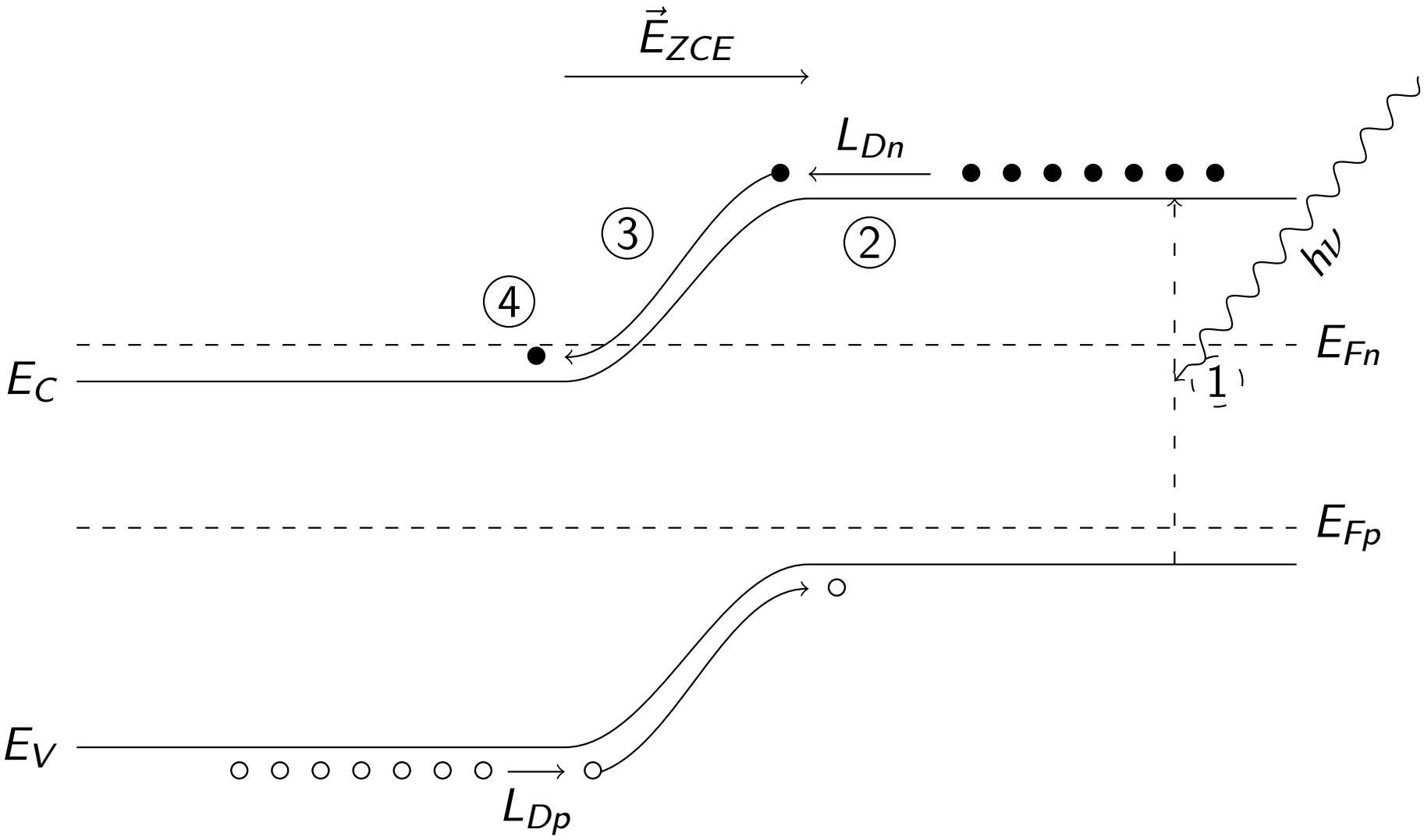
  2. The Common Anion Rule
  3. The Common Cation Rule

Construction of Heterojunction





pn Junction



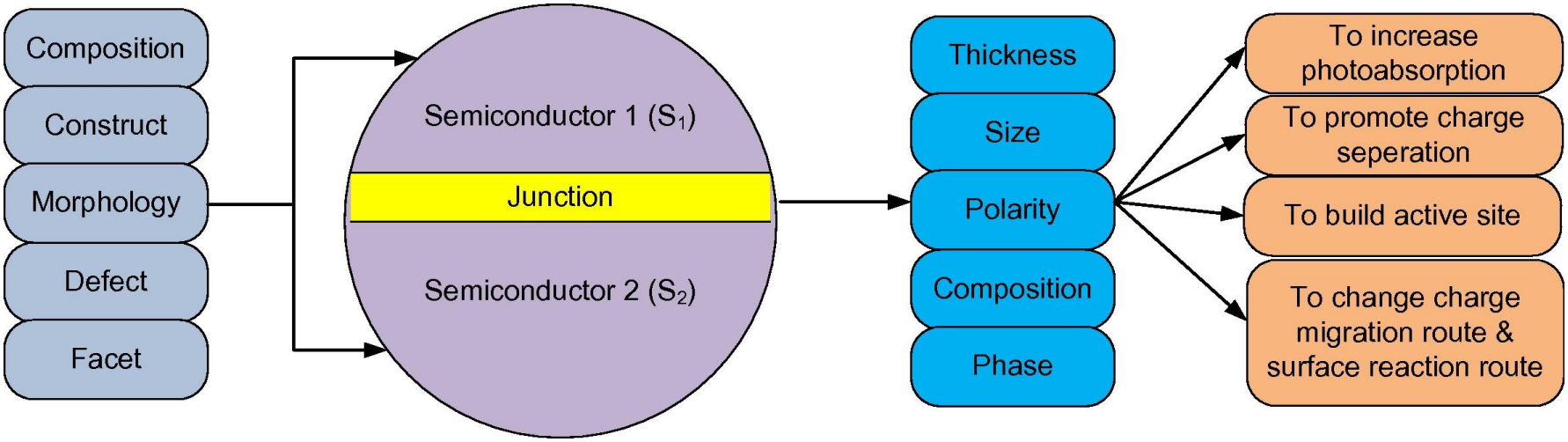
Issues to be Considered

1. Optoelectronic Properties – What are the electronic and optical properties of the two semiconductors under consideration and do they meet the needs of the application?
2. Interface Barriers – What electrostatic fields develop at the heterojunction? Are these compatible with the desired application? A related issue is the presence and nature of defects at the interface that contribute to and modify the resulting fields.
3. Current Flow – It is possible with semiconductor heterojunctions to select for current flow by one charge or the other (electrons or holes) across a junction with less dependence on doping than in the homojunction.

Issues to be Considered

1. Epitaxy – It is possible to grow one semiconductor as a single crystal on another but one must decide upon the best growth method. A nonepitaxial heterojunction will generally have far more interface states than an epitaxial one.
2. Lattice mismatch – If epitaxy is possible any difference of lattice size must be accommodated at the interface and may introduce defects.
3. Interface stability – Do the semiconductors mix across the junction or is the interface thermodynamically stable?
4. Also, we are considering only electronic properties of semiconductor heterojunctions. Optical properties is not be considering at all!

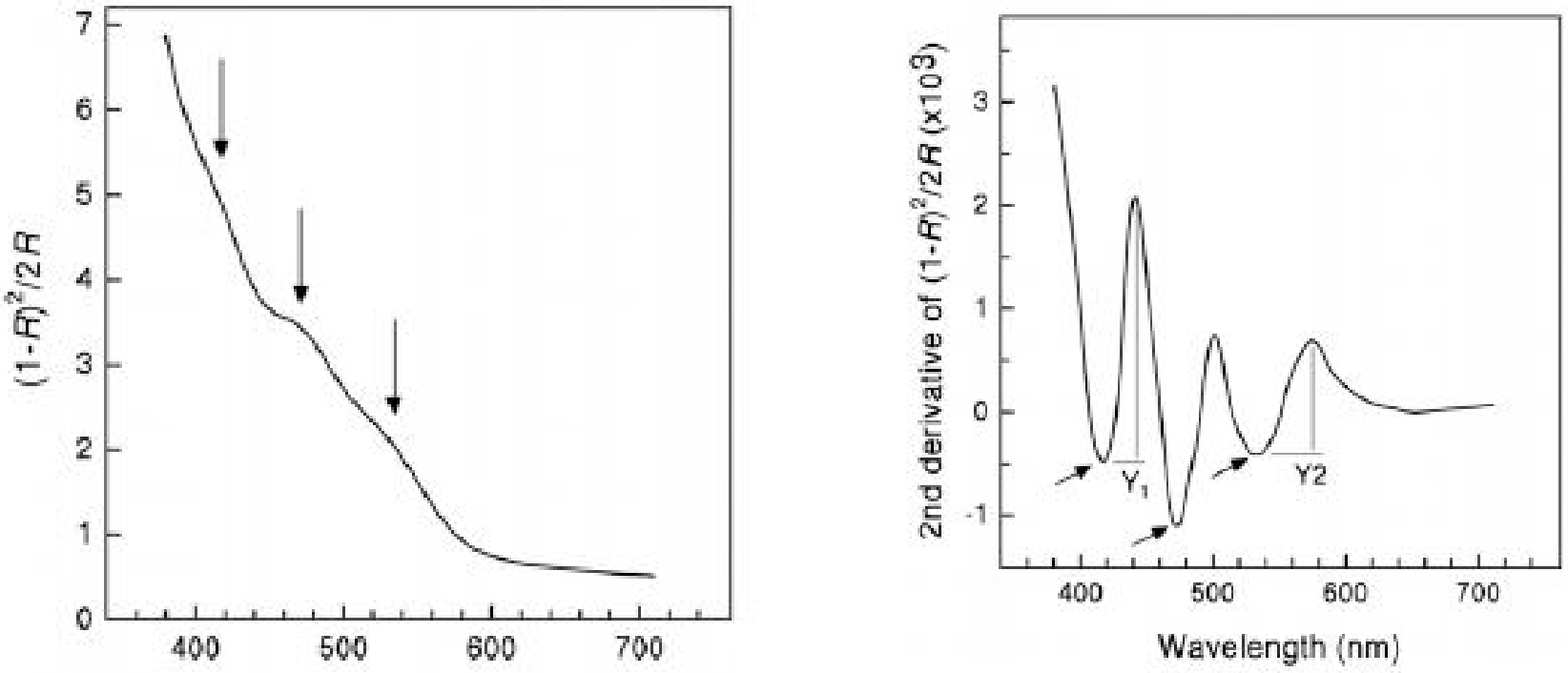
Adjusting and controlling factors of the heterojunction



Characterisation

1. X-Ray Diffraction
2. Photoelectron Spectroscopy, High Resolution Core- and Valence-Level XPS
3. Vibrational Spectroscopy
4. AFM, Atomic Force Microscopy
5. Impedance Spectroscopy
6. Spectroelectrochemical Experiments
7. Pump- Probe Spectroscopy
8. XAFS, XANES
9. Luminescence Spectroscopy
10. Transmission Electron Microscopy
11. Electron Paramagnetic Resonance Spectroscopy

Diffuse Reflectance Spectroscopy



(upper) Kubelka–Munk function spectrum and (lower) its second derivative for a Brazilian Oxisol containing hematite and goethite. The relatively inconspicuous absorption bands (marked with arrows) in the original spectra appear as strong minima in the second-derivative spectrum. The amplitudes of the bands between the minimum at ≈415 nm and the maximum at ≈445 nm (Y1) and between the minimum at ≈535 nm and the maximum ≈580 nm (Y2) were used in the quantitative analysis of these two minerals.

Transmission Electron Microscopy

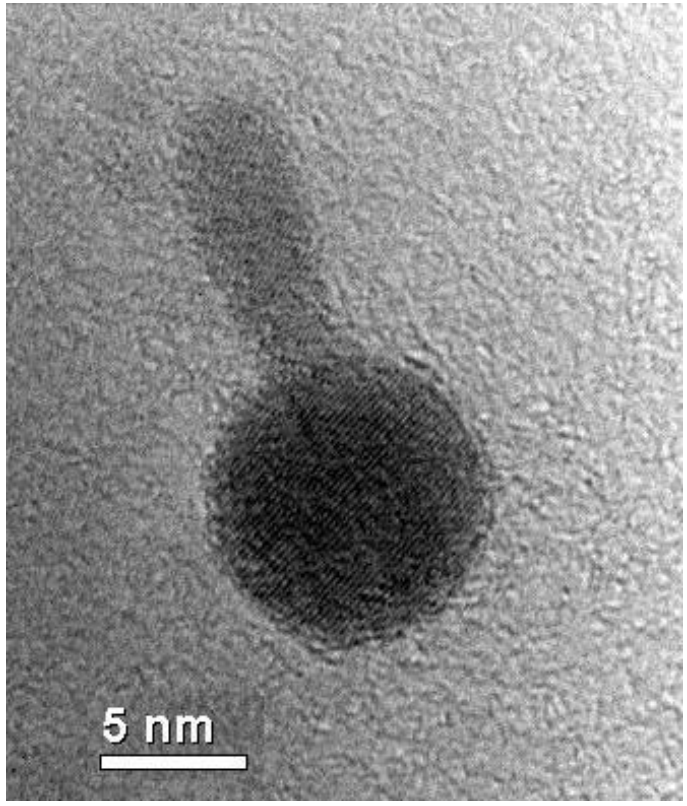


Image of a nanoscale heterojunction between iron oxide (Fe_3O_4 — sphere) and cadmium sulfide (CdS — rod) taken with a TEM. This staggered gap (type II) offset junction was synthesized by Hunter McDaniel and Dr. Moonsub Shim at the University of Illinois in Urbana-Champaign in 2007.

If there is a problem, don't just look at the problem. Look at the reason behind the problem.

Thank You