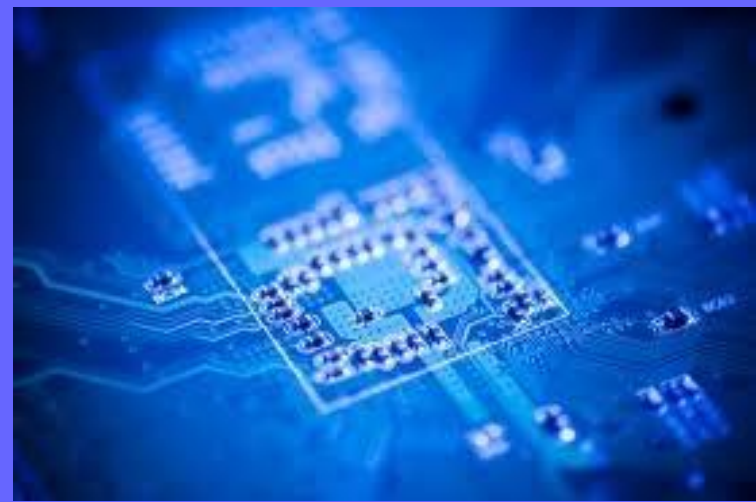
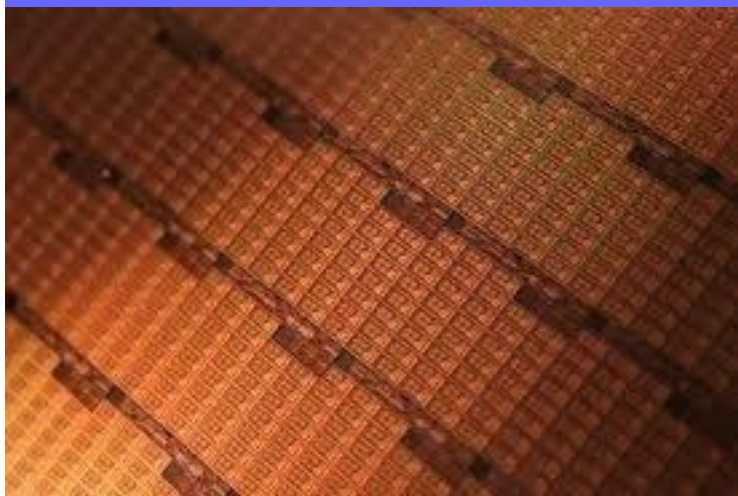


# Chemistry 4631

## Instrumental Analysis

### Lecture 9



# Components of Optical Instruments

## UV to IR

### Basic components of spectroscopic instruments:

- stable source of radiant energy
- transparent container to hold sample
- device to isolate selected region of the spectrum for measurement
- detector to convert radiant energy to a signal
- signal processor and readout

# Components of Optical Instruments

## Photon Transducers

which respond to radiation:

- Phototubes (emission of electrons from a photosensitive solid)
- Photomultiplier tubes
- Photovoltaic cells (current generated at the interface of a semiconductor layer)
- Photoconductivity (production of electrons and holes in a semiconductor)
- Silicon photodiodes (conductance across a reverse bias pn junction)
- Charge transfer (charge develops in silicon crystal)

# Components of Optical Instruments

## Silicon Diode Transducers

**Silicon is a semiconductor.**

A silicon atom has the electronic configuration of  $[\text{Ne}]3s^2p^2$

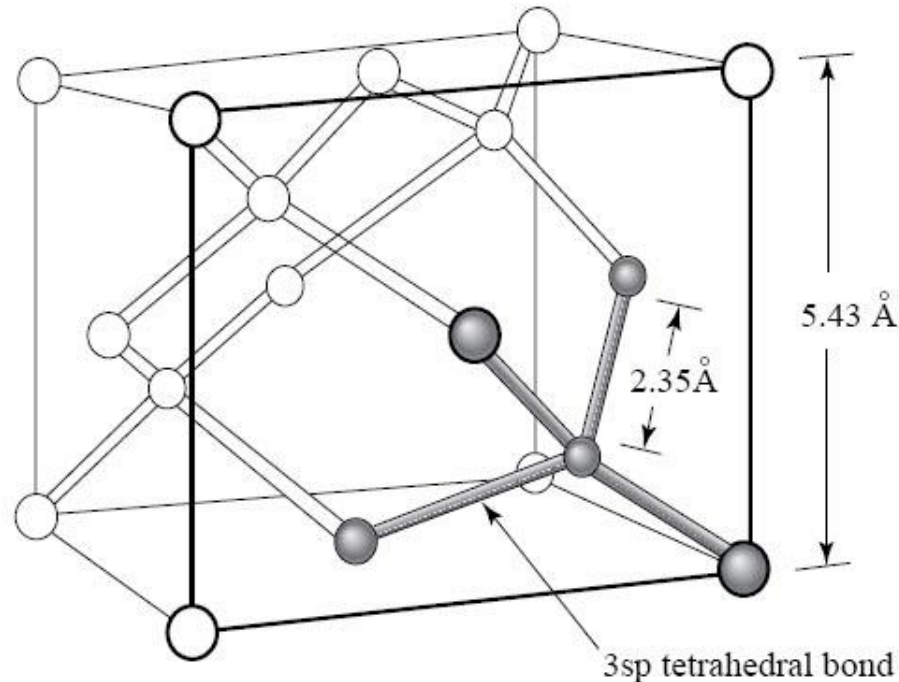
The 3s and 3p however form 4 hybrid orbitals so that silicon can form four bonds.

# Components of Optical Instruments

## Silicon Diode Transducers

### Silicon is a semiconductor.

For a silicon crystal lattice the resulting structure is a tetrahedron arrangement.



# Components of Optical Instruments

## Silicon Diode Transducers

**Silicon is a semiconductor.**

Electronic properties for solids can be described in terms of the band model.

For a crystalline solid, atoms assemble into a lattice forming molecular orbitals.

# Components of Optical Instruments

## Silicon Diode Transducers

### Silicon is a semiconductor.

The filled bonding orbitals form the valence band (VB) and the vacant antibonding orbitals form the conduction band (CB).

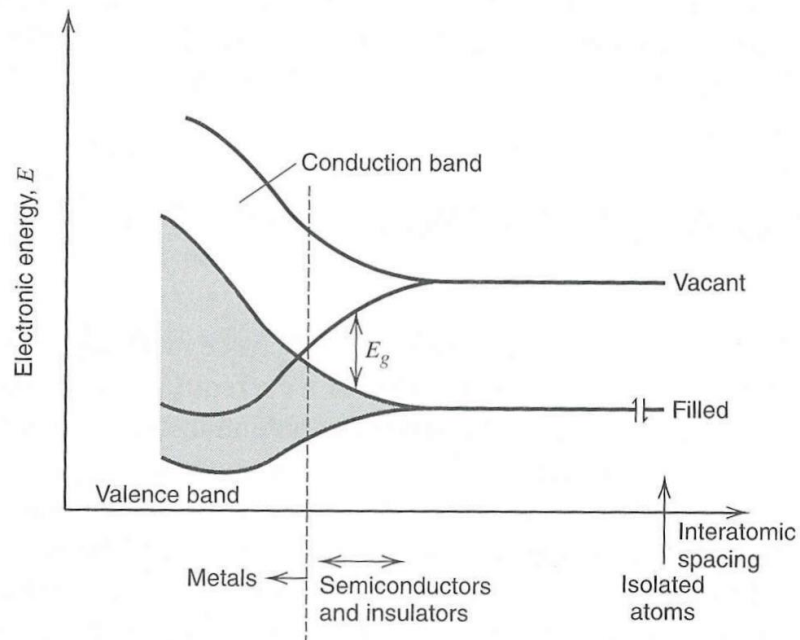
Since the CB is empty – an electron placed in the CB is free to move around.

These bands are separated by a band gap of energy,  $E_g$  (eV).

# Components of Optical Instruments

## Semiconductors

The electrical and optical properties of the solid are strongly influenced by the size of the band gap.



**Figure 18.2.1** Formation of bands in solids (at left) by assembly of isolated atoms (characterized by orbitals at far right) into a lattice.

# Components of Optical Instruments

## Semiconductors

When the gap is very small ( $E_g \ll kT$ ) or the conduction and valence bands overlap, the material is a good conductor.

For larger values of  $E_g$  (i.e. Si, 1.1 eV), valence band is almost filled and conduction band is almost vacant, then semiconductor.

# Components of Optical Instruments

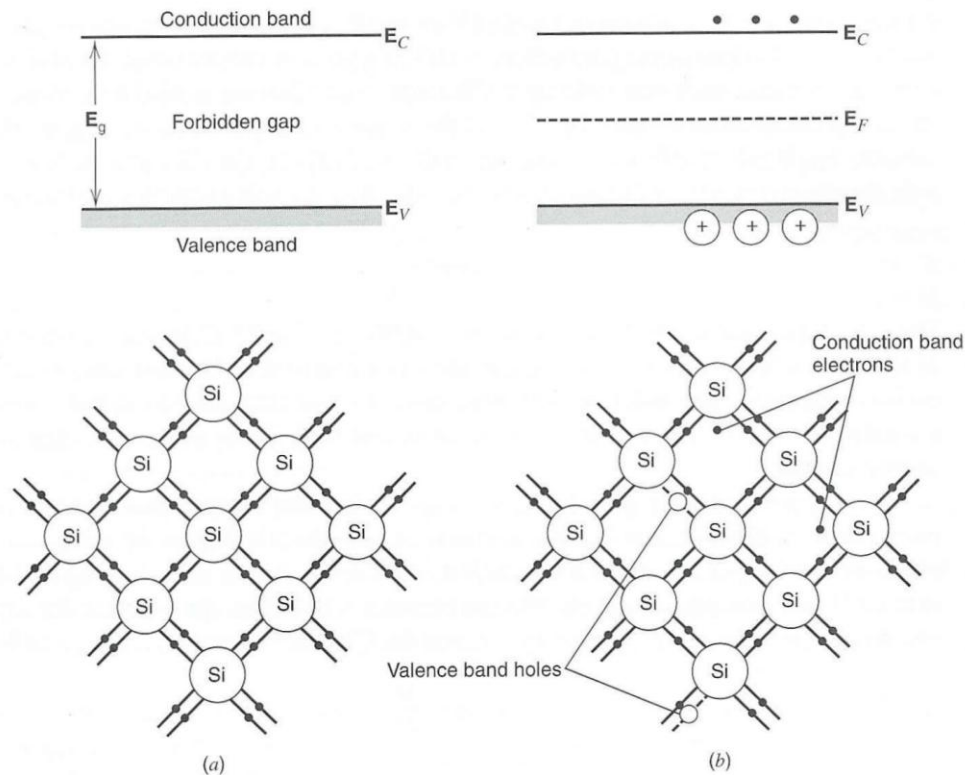
## Semiconductors

Conduction occurs by thermal excitation of electrons from VB into the CB, producing electrons in CB and “holes” in VB.

The charge can then be carried by the electrons and holes.

This is called an intrinsic semiconductor.

# Components of Optical Instruments



**Figure 18.2.2** Energy bands and two-dimensional representation of an intrinsic semiconductor lattice. (a) At absolute zero (or  $E_g \gg kT$ ), assuming a perfect lattice; no holes or electrons exist. (b) At a temperature where some lattice bonds are broken, yielding electrons in the conduction band and holes in the valence band.  $E_F$  represents the Fermi level in this intrinsic semiconductor.

# Components of Optical Instruments

## Semiconductors

For an intrinsic semiconductor, the electrons and hole densities are equal.

$n_i$  – density for CB electrons

$p_i$  – density for VB holes

$$n_i p_i = (\text{constant}) \exp(-E_g/kT)$$

# Components of Optical Instruments

## Semiconductors

$$n_i = p_i = 2.5 \times 10^{19} \exp(-E_g/2kT) \text{cm}^{-3} \text{ (near } 25^\circ\text{C)}$$

The mobile carriers move in the semiconductor and have mobilities of

$$u_n = 1350 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \text{ and } u_p = 480 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$$

An intrinsic semiconductor is a pure semiconductor crystal in which the electron and hole concentrations are equal.

# Components of Optical Instruments

## Semiconductors

However, electrons in CB and holes in VB can be introduced by adding dopants into the semiconductor lattice to produce an extrinsic semiconductor.

This causes the concentration of one of the carriers to be in excess of the other.

# Components of Optical Instruments

## Semiconductors

Example: Add As atoms (Group V) which behave as electron donor for silicon (Group IV) and introduce an energy level,  $E_D$  just below the CB.

Thus at room temperature, the donor atoms are ionized and give a CB electron leaving a positive site.

# Components of Optical Instruments

## Semiconductors

Example: Add As atoms (Group V) which behave as electron donor for silicon (Group IV) and introduce an energy level,  $E_D$  just below the CB.

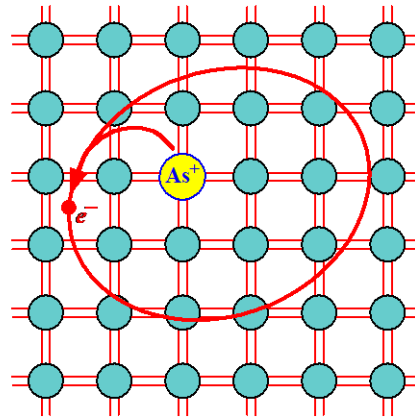
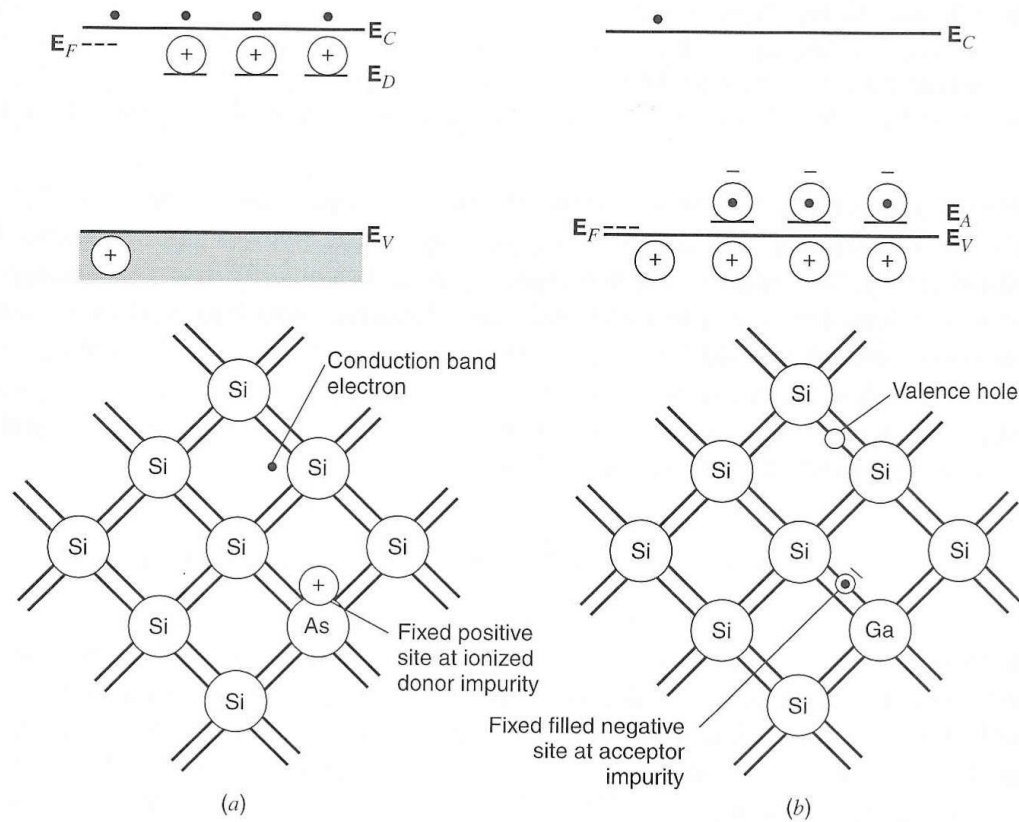


Fig. 5.9: Arsenic doped Si crystal. The four valence electrons of As allow it to bond just like Si but the fifth electron is left orbiting the As site. The energy required to release to free fifth-electron into the CB is very small.

# Components of Optical Instruments



**Figure 18.2.3** Energy bands and two-dimensional representation of extrinsic semiconductor lattices. (a) *n*-type. (b) *p*-type.

# Components of Optical Instruments

## Semiconductors

For 1 ppm of added dopant – the donor density is  $N_D = 5 \times 10^{16} \text{ cm}^{-3}$  – making up most of the CB electron density,  $n$ .

$$p = n_i^2 / N_D$$

In this case, the electrical conductivity is attributed to the CB electrons and are called the majority carriers.

Thus a material doped with a donor atom is called a n-type semiconductor.

# Components of Optical Instruments

## Semiconductors

Example: Add Ga atoms (Group III) which is an acceptor atom to silicon (Group IV) then introduce an energy level  $E_A$  just above VB.

Thus at room temperature, the electrons are thermally excited from the VB into the acceptor sites leaving mobile holes in the VB.

# Components of Optical Instruments

## Semiconductors

Example: Add Ga atoms (Group III) which is an acceptor atom to silicon (Group IV) then introduce an energy level  $E_A$  just above VB.

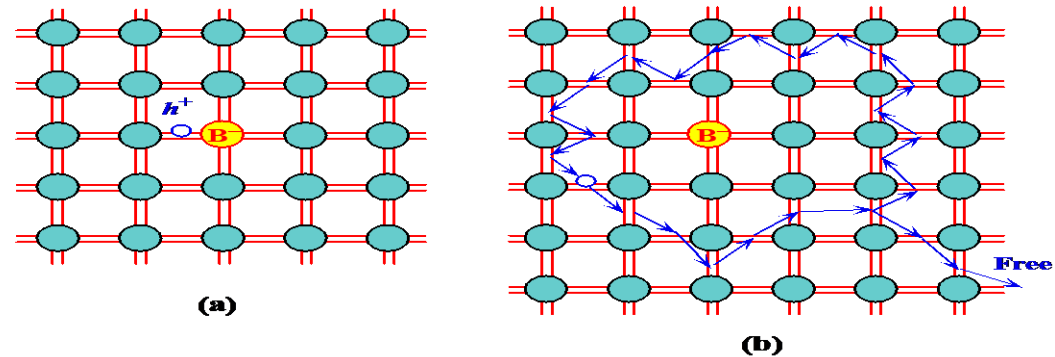
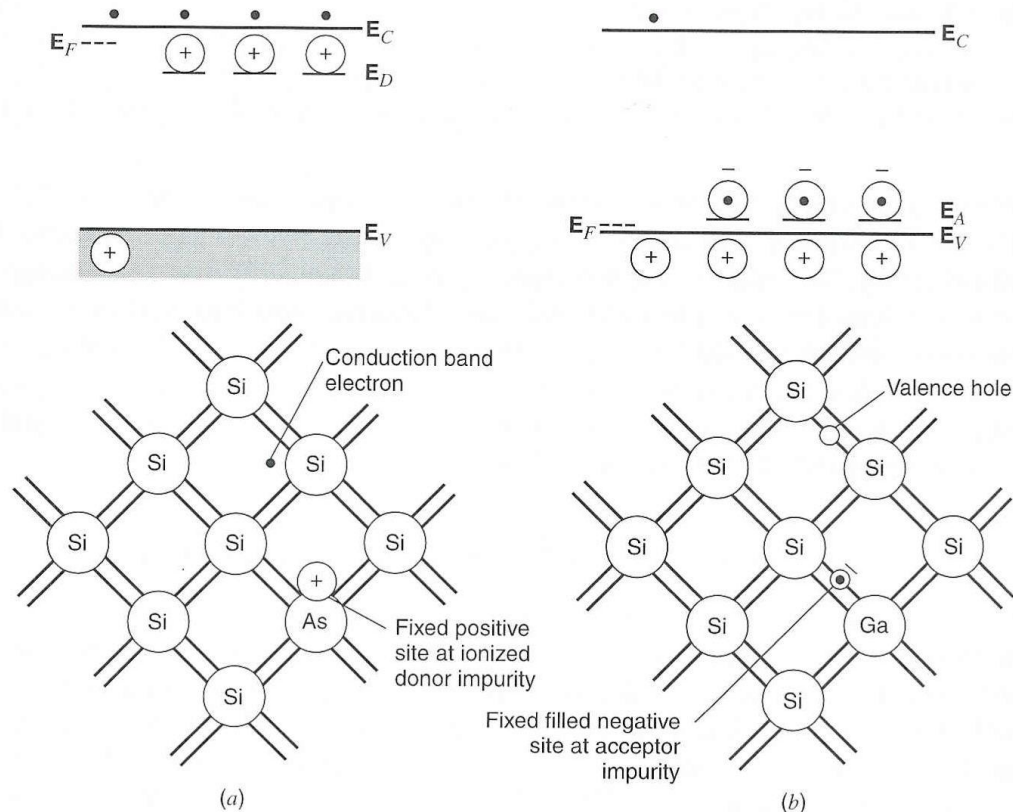


Fig. 5.11: Boron doped Si crystal. B has only three valence electrons. When it substitutes for a Si atom one of its bonds has an electron missing and therefore a hole as shown in (a). The hole orbits around the B– site by the tunneling of electrons from neighboring bonds as shown in (b). Eventually, thermally vibrating Si atoms provides enough energy to free the hole from the B– site into the VB as shown.

# Components of Optical Instruments



**Figure 18.2.3** Energy bands and two-dimensional representation of extrinsic semiconductor lattices. (a) *n*-type. (b) *p*-type.

# Components of Optical Instruments

## Semiconductors

Acceptor density,  $N_A$  makes up most of the hole density,  $p$ .

$$n = p_i^2 / N_A$$

In this case, the electrical conductivity is attributed to the holes as the majority carriers and the material is called a p-type semiconductor.

# Components of Optical Instruments

## Silicon semiconductor

The conductivity of silicon can be enhanced by doping the Si with As (Group V) or Ga (Group III).

As has 5 e's, with 4 forming bonds with silicon, leaving an extra electron to travel through the crystal. (n-type)

Ga has 3 e's leaving an excess of holes (+ charge) to act as mobile carriers in the crystal. (p-type)

# Components of Optical Instruments

## Semiconductors

### Optical Absorption

When a photon of energy higher than  $E_g$  strikes a semiconductor, electrons are excited from the VB to the CB.

# Components of Optical Instruments

## Semiconductors

### Optical Absorption

Beer-Lambert Law for the semiconductor:

$$I(x) = I_0 \exp(-\alpha x)$$

where

$I(x)$  – transmitted intensity

$I_0$  – intensity of photons incident on semiconductor

$\alpha$  – absorption coefficient of the semiconductor

$x$  – thickness

The distance over which 67 percent of the photons are absorbed is called the penetration depth.

# Components of Optical Instruments

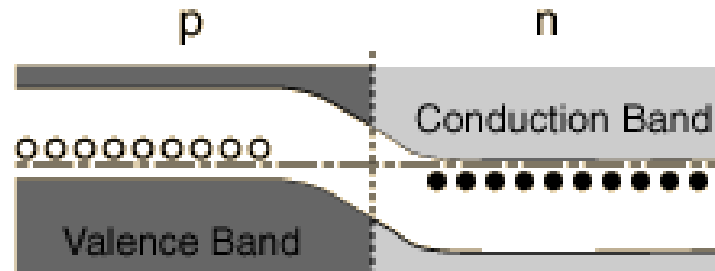
## Semiconductors pn junctions

Formed by contact between a p-type and n-type semiconductor.

The junction formed has rectifying properties – current can flow in one direction easily but limited in the other direction.



p-n junction



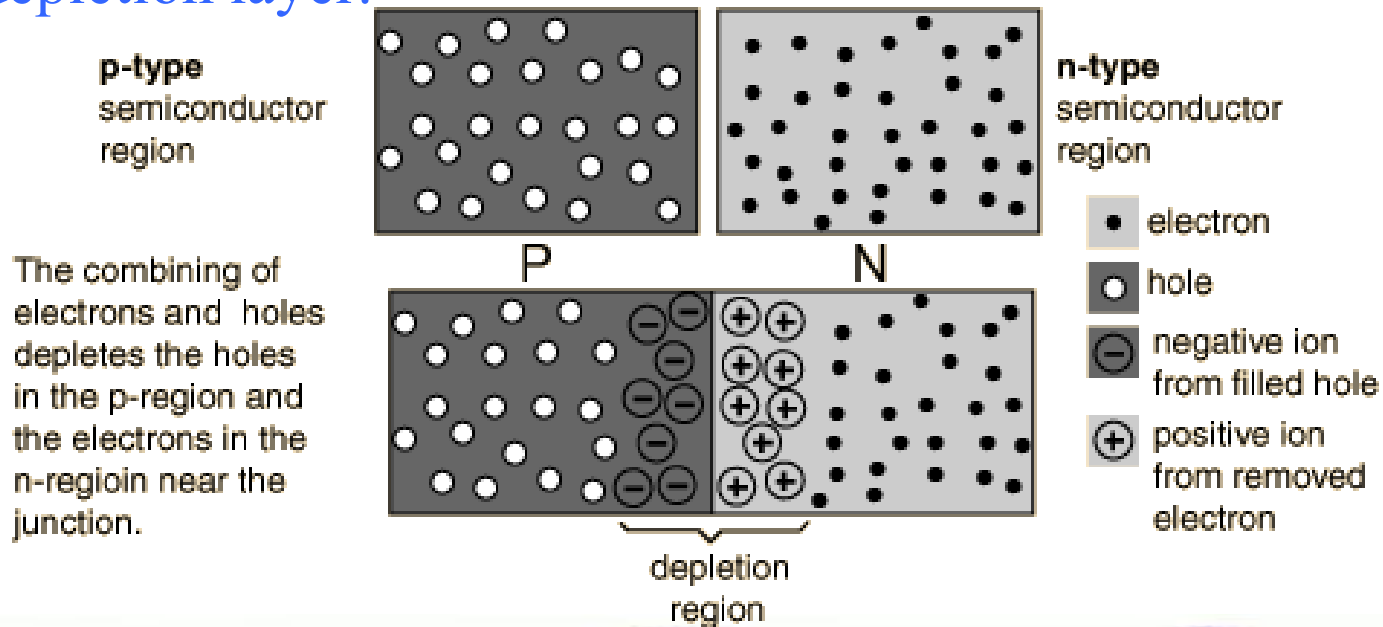
Energy bands at equilibrium

# Components of Optical Instruments

## Semiconductors

### pn junctions

When the pn junction forms - some of the free electrons at the interface diffuse and combine with the holes creating a depletion layer.



# Components of Optical Instruments

## Semiconductors

### pn junctions

When the electron and hole recombine this process is called recombination.

In some semiconductors, i.e. GaAs and InP this process results in an emission of a photon. This is a direct recombination mechanism and the excess energy of the electron is lost as a photon  $h\nu = E_g$ .

In other semiconductors, the energy is simply lost as lattice vibrations (heat).

# Components of Optical Instruments

## Semiconductors

### pn junctions

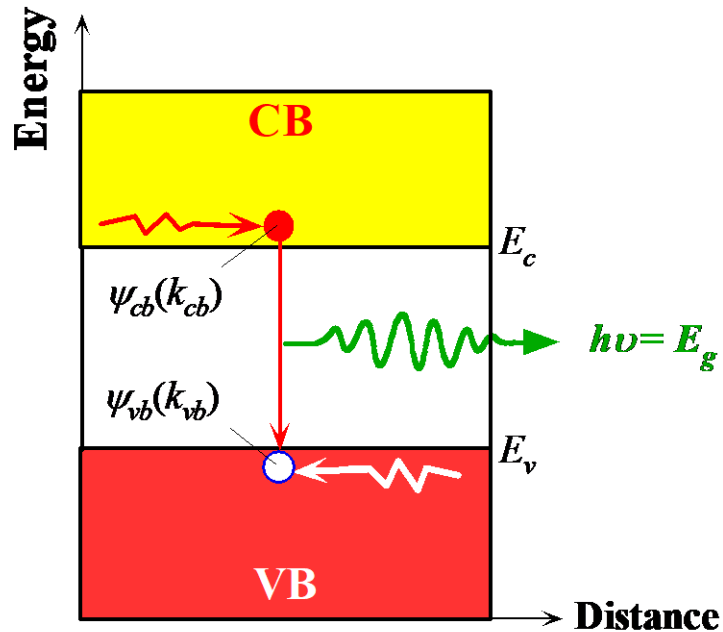


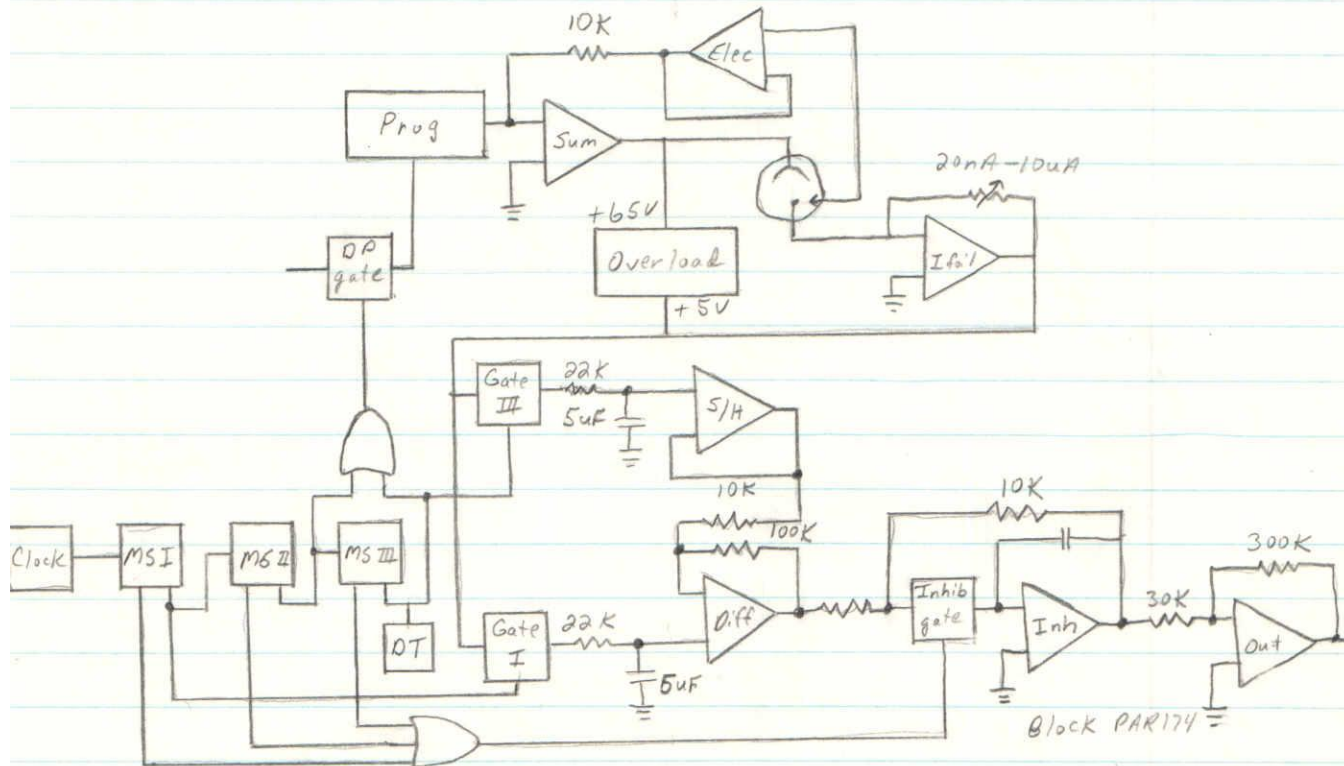
Fig.5.22: Direct recombination in GaAs.  $k_{cb} = k_{vb}$  so that momentum conservation is satisfied

# Assignment

- Read Chapter 7
- Read Chapter 13
- HW4 Chapter 13: 1, 2, 5-8, 12, 13, 16-19
- HW4 Chapter 13 Due 2-6
- Exam 1- Lectures 1 to 8 - Friday Feb 6<sup>th</sup>

# Instrument Lab

Block diagram of EG+G PARC Model 174A  
Polorographic Analyzer (Instrumental Method  
of Analysis, 6<sup>th</sup> Ed, Dean & Settle)



# Instrument Lab

## II. Instrumentation

The Instrument used was a Spectrophotometer Beckman Double Beam # 14011100834. And the light source was a Beckman Hydrogen Lamp Power Supply # 337997.

Schematic drawing: Figure 1: Double Beam Spectrometer

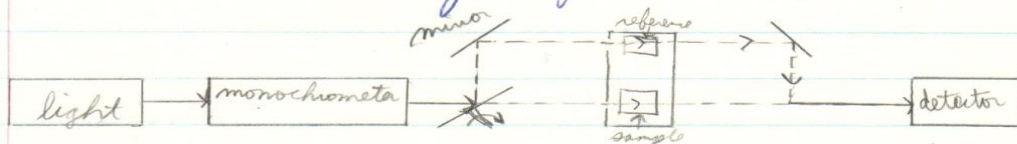


Figure 2: A scanning double-beam spectrometer with dual source, single grating.  
pg. 57, Instrumental Analysis, Dean & Settle

