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

Detectors

Photon detectors are classified as either photocurrent or photoconduction detectors.

Components of Optical Instruments

Detectors (response to photons (x-rays))

- 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)
- Photodiode Array (silicon photodiodes)
- Charge transfer (charge develops in silicon crystal)
- Charge coupled
- Charge injection

Components of Optical Instruments

Detectors

Photoconduction detectors are based on semiconductor technology.

Components of Optical Instruments

Detectors

Photovoltaic (Barrier-Layer) Cells

- for vis region
- Maximum sensitivity is at ~ 550 nm
- Range from ~ 350 to 750 nm
- Made up of a Cu or Fe electrode with a layer of semiconducting material.
- Semiconductor coated with thin transparent metallic film of Au or Ag to serve as collector electrode.

Components of Optical Instruments

Photovoltaic (Barrier-Layer) Cells

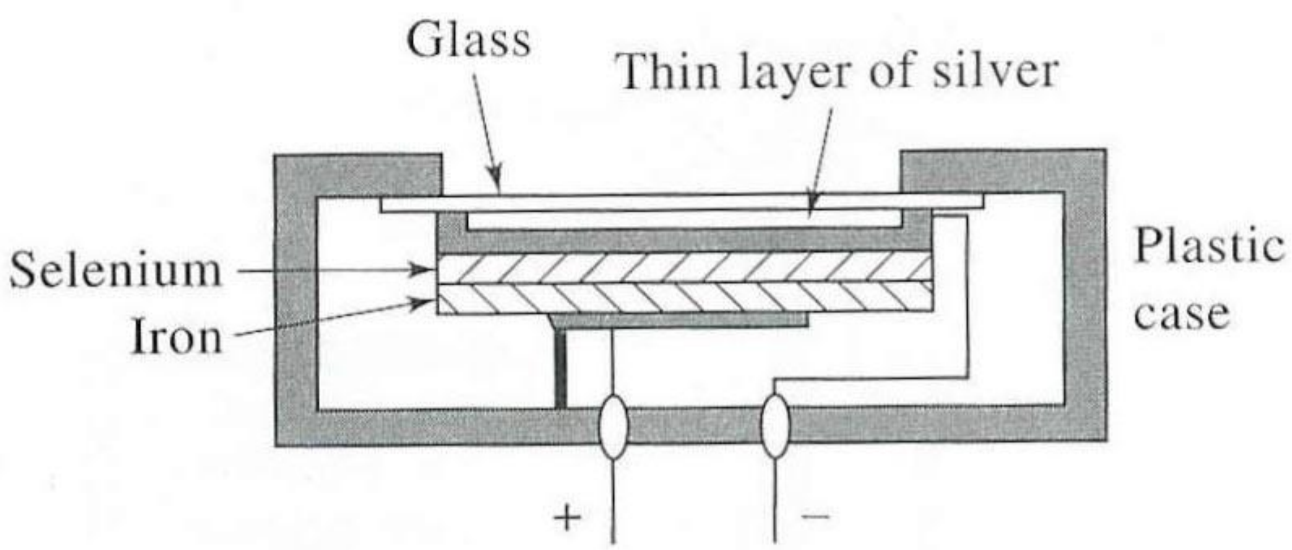

Figure 7-26 Schematic of a typical barrier-layer cell.

Components of Optical Instruments

Photovoltaic (Barrier-Layer) Cells

Radiation of appropriate energy strikes the semiconductor breaking covalent bonds and forming conduction electrons and holes.

Electrons migrate toward metallic film and holes toward the base.

Components of Optical Instruments

Photovoltaic (Barrier-Layer) Cells

Current proportional to the number of photons striking surface, 10 – 100 μA.

Disadvantages:

- Low sensitivity
- Exhibits fatigue

Advantages:

- Simple
- Rugged
- Low cost

Components of Optical Instruments

Detectors (response to photons)

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Components of Optical Instruments

Silicon Diode Transducers

A reverse-biased pn junction (pn diode) on a silicon chip can be fabricated to act as a detector.

When a reverse-bias is applied, a depletion layer forms.

Components of Optical Instruments

Silicon Diode Transducers

UV and vis photons have enough energy to create holes or electrons when striking the depletion layer of a pn junction.

The holes and electrons formed in the depletion layer migrate to the connecting leads and produce a current.

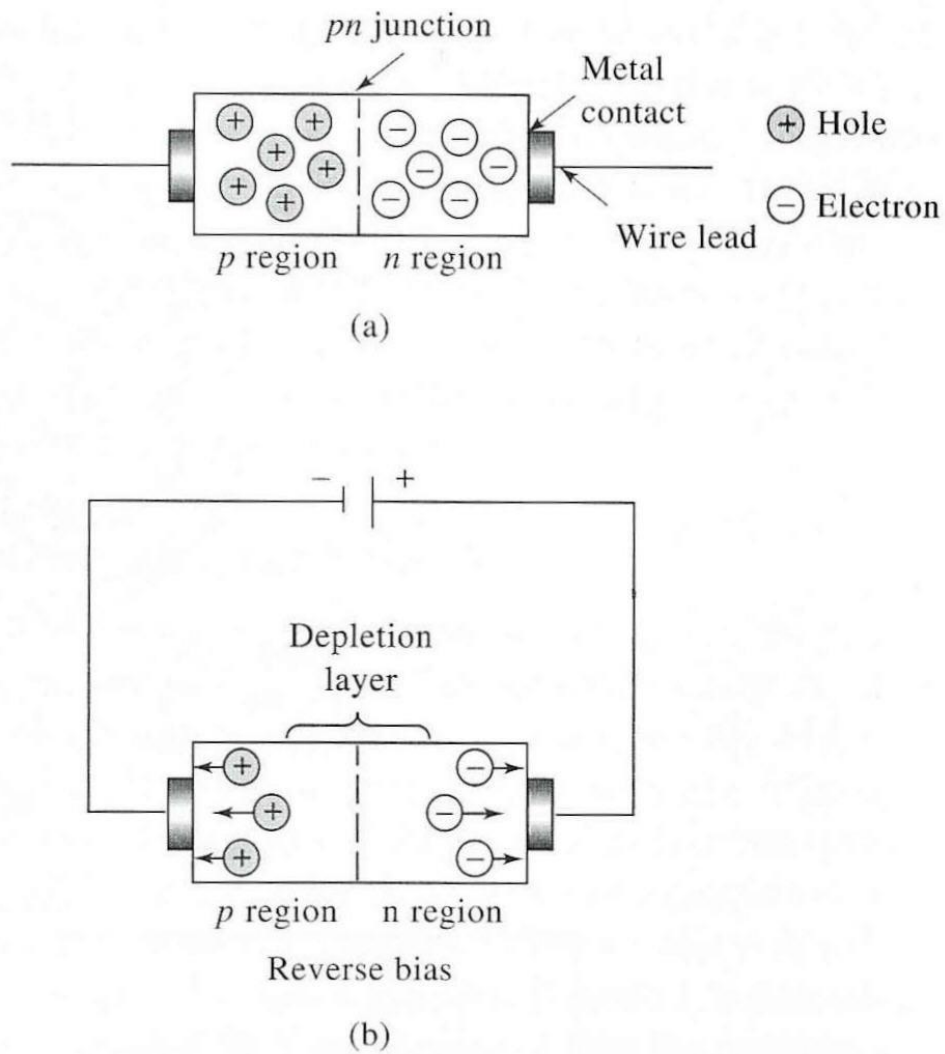


Figure 7-30 (a) Schematic of a silicon diode. (b) Formation of depletion layer, which prevents flow of electricity under reverse bias.

Components of Optical Instruments

Silicon Diode Transducers

The spectral range: 190 to 1100 nm

Spectral response - an important characteristic of any photo-detector.

Measures how the photocurrent, varies with the wavelength of incident light.

Components of Optical Instruments

Silicon Diode Transducers

Frequency response - measures how rapidly the detector can respond to a time varying optical signal.

The generated minority carriers have to diffuse to the depletion region before an electrical current can be observed externally.

Since diffusion is a slow process, the maximum frequency response is a few tens of MHz for pn junctions. Higher frequency response (a few GHz) can be achieved using p-i-n diodes.

Components of Optical Instruments

Silicon Diode Transducers

(p-i-n and avalanche photodiodes)

A silicon photodiode designed with gain – uses relatively high reverse bias (10-100 V) to accelerate electrons through the crystal lattice and create more through impact ionization.

The i-region is very lightly doped (it is effectively intrinsic).

The diode is designed such that most of the light is absorbed in the i-region.

Components of Optical Instruments

Silicon Diode Transducers

(p-i-n and avalanche photodiodes)

Under reverse bias, the i-region is depleted, and the carriers generated in the i-region are collected rapidly due to the strong electric field.

p-i-n diodes operating at 1.3 μm and 1.55 μm are used extensively in optical fiber communications.

However arrays of avalanche photodiodes are approaching gains of PMTs and called silicon photomultipliers (SiPMs).

SiPMs – gain = 10^6, efficiency = 20-50%, rapid response, UV-IR range, more compact, single photon counting.

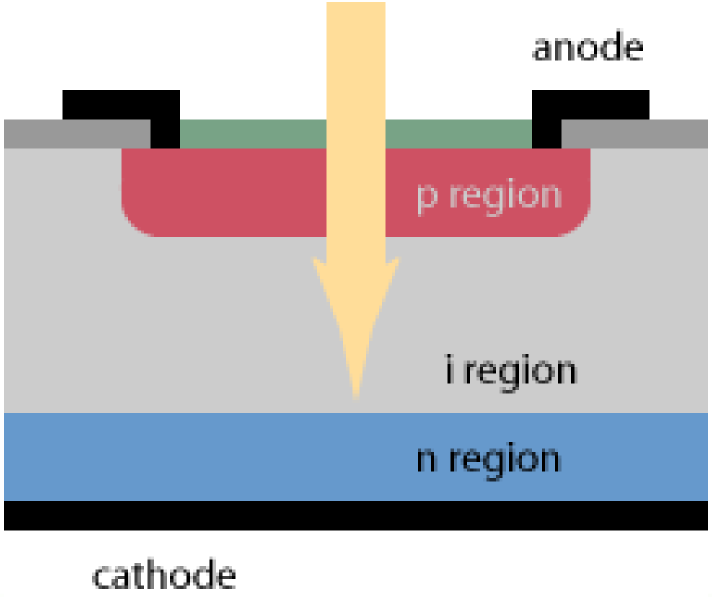
Components of Optical Instruments

Silicon Diode Transducers

p-i-n photodiode has a thicker depletion region to allow for more efficient collection of carriers and higher quantum efficiency.

Example: p-i-n photodiodes operating at 1.55 um made of $In_{0.53}Ga_{0.47}As$ deposited on InP substrate.

Noise in a p-i-n photodiode (or p-n) is primarily due to shot noise; the random nature of the generation of carriers in the photodiode yields also a random current fluctuation.



Components of Optical Instruments

Detectors (response to photons)

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Components of Optical Instruments

Multichannel Photon Transducers

Consist of an array of small photoelectric-sensitive elements arranged in a pattern on a chip.

Three types:

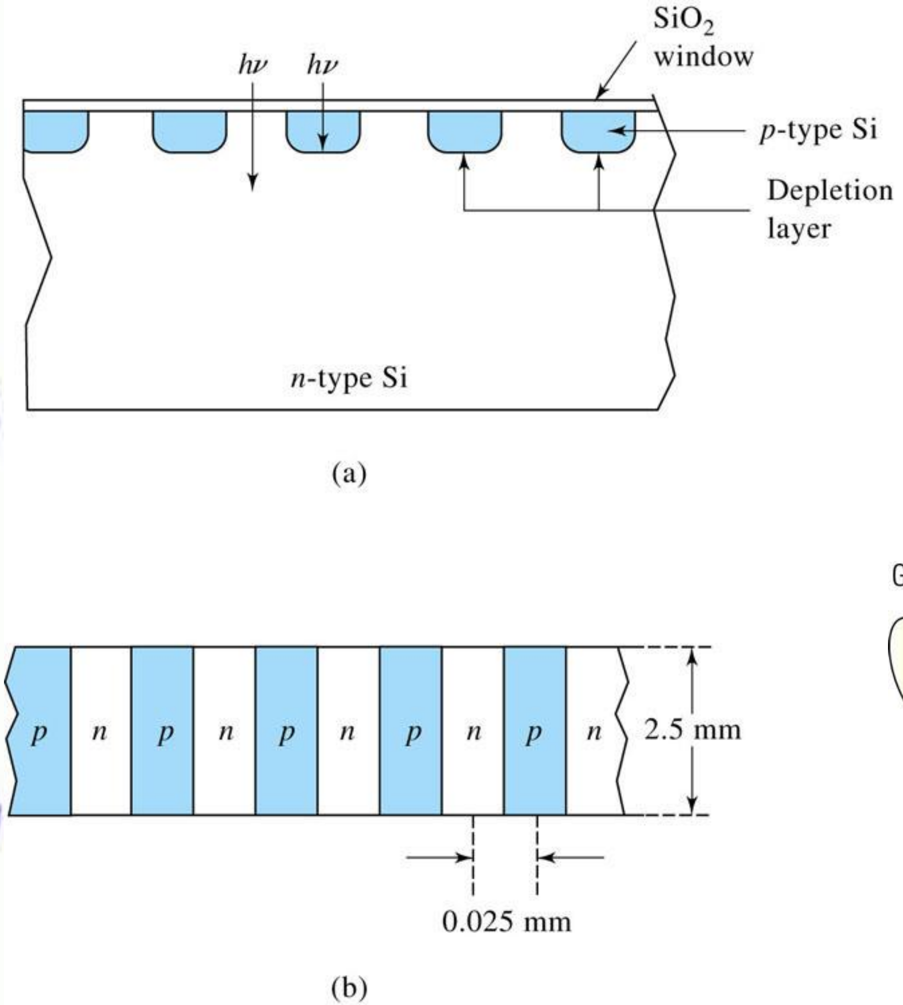
- Photodiode arrays (PDAs)
- Charge-injection devices (CIDs)
- Charge-coupled devices (CCDs)

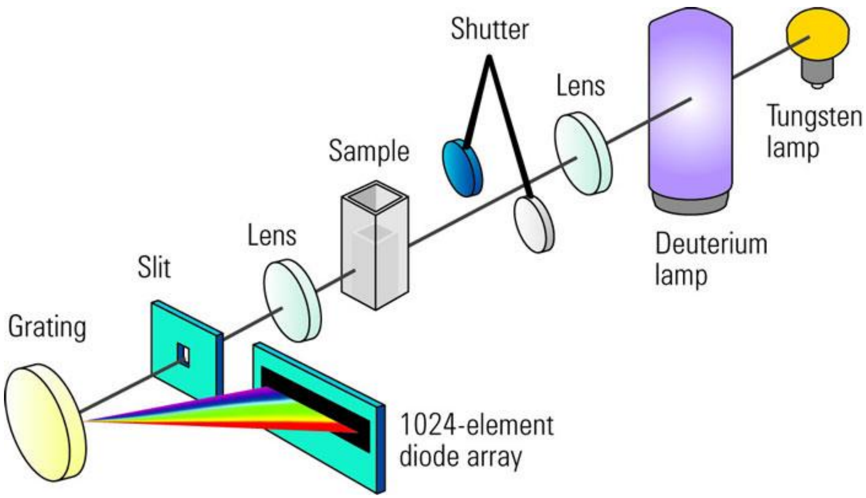
Components of Optical Instruments

Photodiode Arrays (PDAs)

Small silicon photodiodes which contain reverse-biased pn junctions.
Number on a chip ~ 64 to 4096.
Not as sensitive as PMTs.
Less dynamic range than PMTs.

Components of Optical Instruments



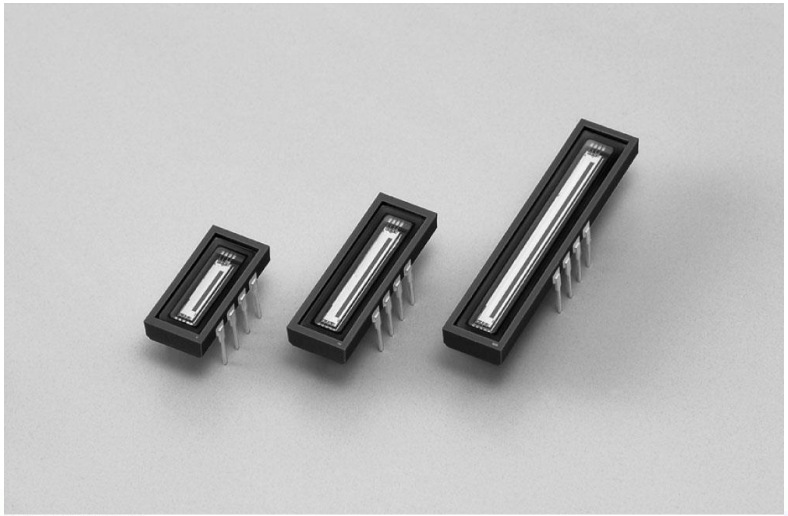


Components of Optical Instruments

Photodiode Arrays (PDAs)

The transducer (chip) consist of a linear array of several hundred photodiodes (256, 512, 1024, 2048).

The chip is 1 – 6 cm in length and individual diode widths are 15 – 50 mm. Each diode has a capacitor and an electronic switch.



Components of Optical Instruments

Photodiode Arrays (PDAs)

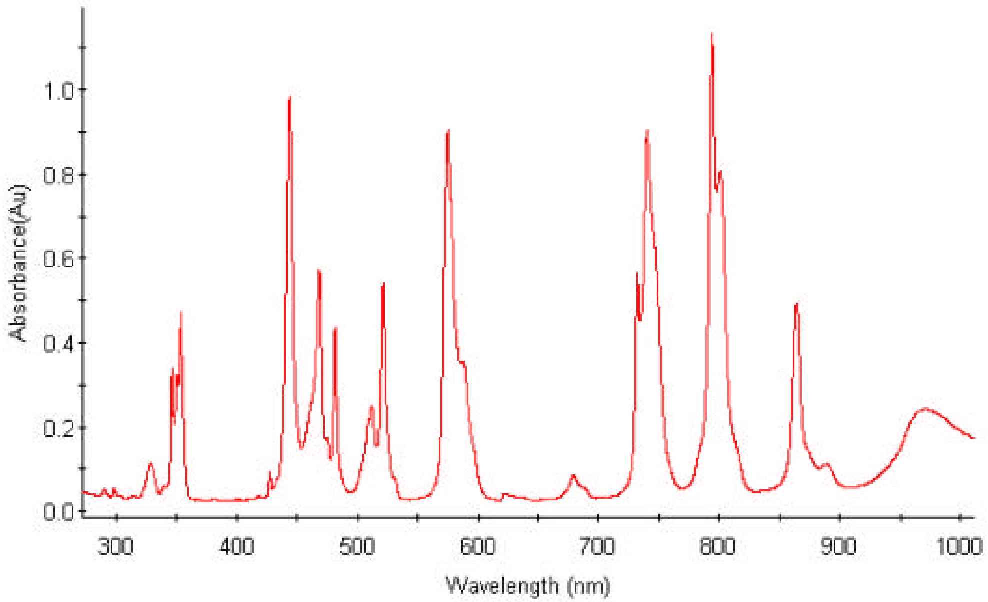
Advantages

- Simultaneous Multiwavelength Measurement
- Fast Scan Speed
- High Signal to Noise Ratio
- Wavelength Precision
- Minimal Stray Light effects
- Ruggedness

Components of Optical Instruments

Photodiode Arrays (PDAs)

Simultaneous Multi wavelength Measurement



The spectrum of didymium solution: S-3150, SCINCO, measuring time 1 sec.

Components of Optical Instruments

Detectors (response to photons)

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Components of Optical Instruments

Charge-Transfer Devices CTDs (CIDs and CCDs)

- Performance closer to PMTs
- Additional advantage – can do multichannel measurements
- Can record 2-D spectrum from an echelle spectrometer

Components of Optical Instruments

Charge-Transfer Devices CTDs

Amount of charge generated from a radiation strike can be measured by 2 ways:

CIDs - the voltage change that arises form movement of the charge from under one electrode to another is measured.

CCDs – the charge is moved to a charge-sensing amplifier for measurement.

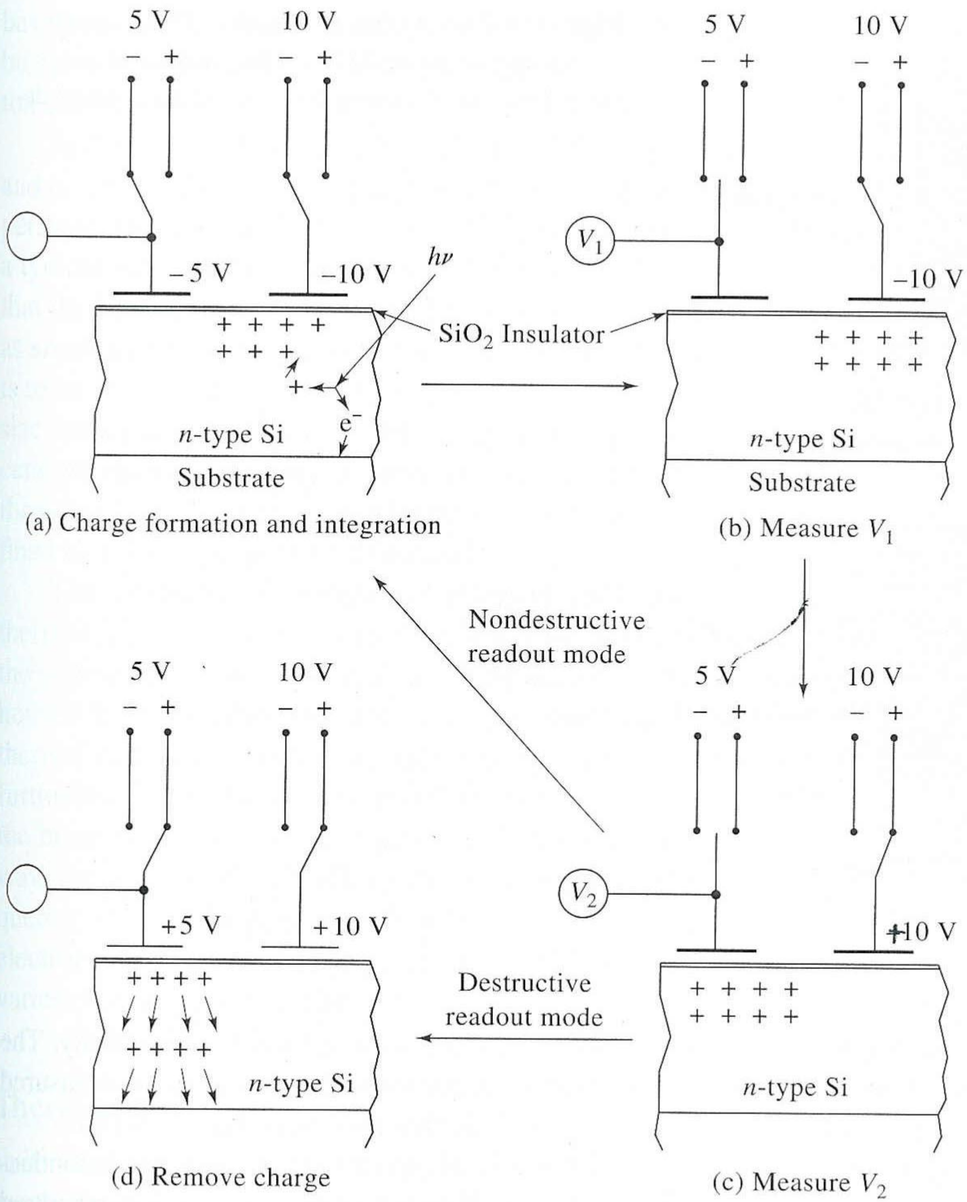


Figure 7-34 Duty cycle of a charge-injection device: (a) production and storage of charge, (b) first charge measurement, (c) second charge measurement after charge transfer, (d) reinjection of charge into the semiconductor.

Components of Optical Instruments

Charge-Coupled Devices (CCDs)

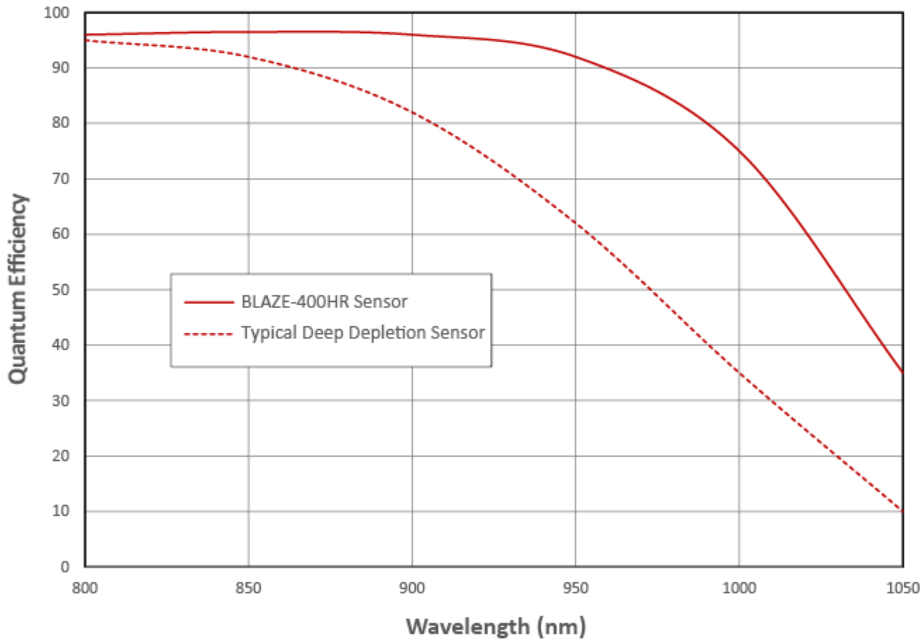
Typical array 512 x 320 pixels

- Semiconductor is formed from p-type silicon capacitor
- Capacitor is positively biased
- Electrons formed by the absorption of radiation collected in a well below the electrode

Components of Optical Instruments

Charge-Coupled Devices (CCDs)

Linear CCD arrays and cameras are available with pixels as great as 12,000 to give very high resolution.

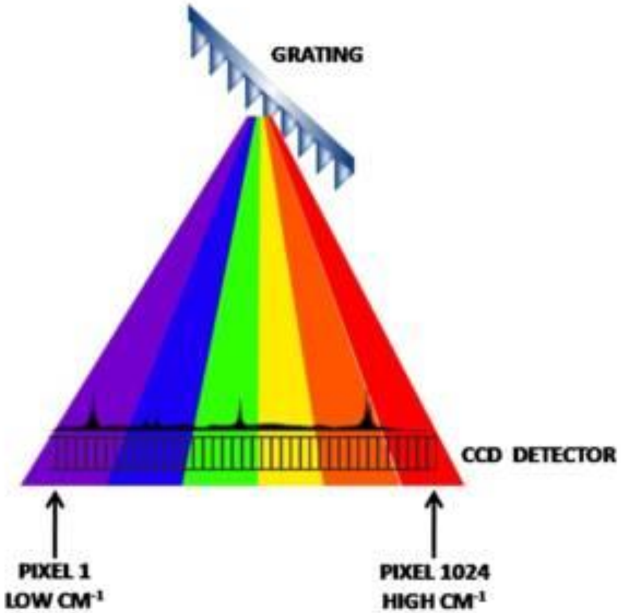


Components of Optical Instruments

Charge-Coupled Devices (CCDs)

Scattered light is dispersed using the diffraction grating, and this dispersed light is then projected onto the long axis of the CCD array.

The first element will detect light from the low cm^{-1} edge of the spectrum, the second element will detect light from the next spectral position, and so on...



Components of Optical Instruments

Charge-Coupled Devices (CCDs)

CCDs require some degree of cooling to make them suitable for high grade spectroscopy.

Typically this is done using either peltier cooling (suitable for temperatures down to -90^{o}C), or liquid nitrogen cryogenic cooling.

The Peltier effect is used in detectors for cooling.

One of three reversible thermoelectric phenomena, often known simply as thermoelectric effects.
The other two are the Seebeck effect and the Thomson effect.

Components of Optical Instruments

Charge-Coupled Devices (CCDs)

The Peltier effect is a creation of a heat difference from an electric voltage.

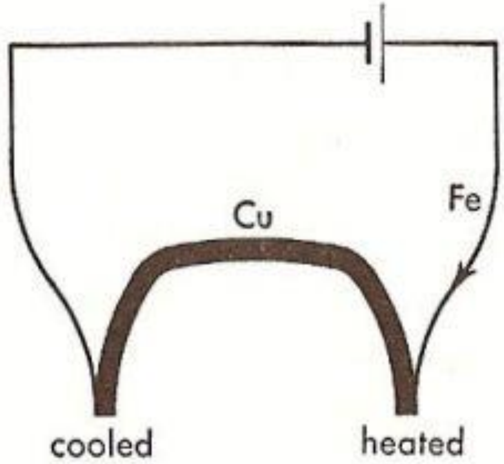
This effect was observed in 1834 by Jean Peltier.

Peltier found that the junctions of dissimilar metals were heated or cooled, depending upon the direction in which an electrical current passed through them.

Components of Optical Instruments

Peltier effect

Heat generated by current flowing in one direction was absorbed if the current was reversed.
The Peltier effect is found to be proportional to the first power of the current, not to its square, as is the irreversible generation of heat caused by resistance throughout the circuit.



Components of Optical Instruments

Peltier effect

The Peltier effect can also occur when a current is passed through two dissimilar semiconductors (n-type and p-type) that are connected to each other at two junctions (Peltier junctions).

The current drives a transfer of heat from one junction to the other: one junction cools off while the other heats up; as a result, the effect is often used for thermoelectric cooling.

An interesting consequence of this effect is that the direction of heat transfer is controlled by the polarity of the current; reversing the polarity will change the direction of transfer and thus the sign of the heat absorbed/evolved.

A Peltier cooler/heater or thermoelectric heat pump is a solid-state active heat pump which transfers heat from one side of the device to the other. Peltier coolers are also called thermo-electric coolers (TEC).

Components of Optical Instruments

Detectors

For measurement in IR region

Three general types:

- Thermal
- Pyroelectric
- Photoconductivity

Components of Optical Instruments

Thermal Transducers

Radiation is absorbed by a small blackbody and the temperature rise is measured. Radiant power from the beam is 10^{-7} to 10^{-9} W, so heat capacity of absorbing element must be small.

Temperature changes are ~ 0.001 Kelvin.

Components of Optical Instruments

Thermal Transducers

Thermal noise is biggest drawback

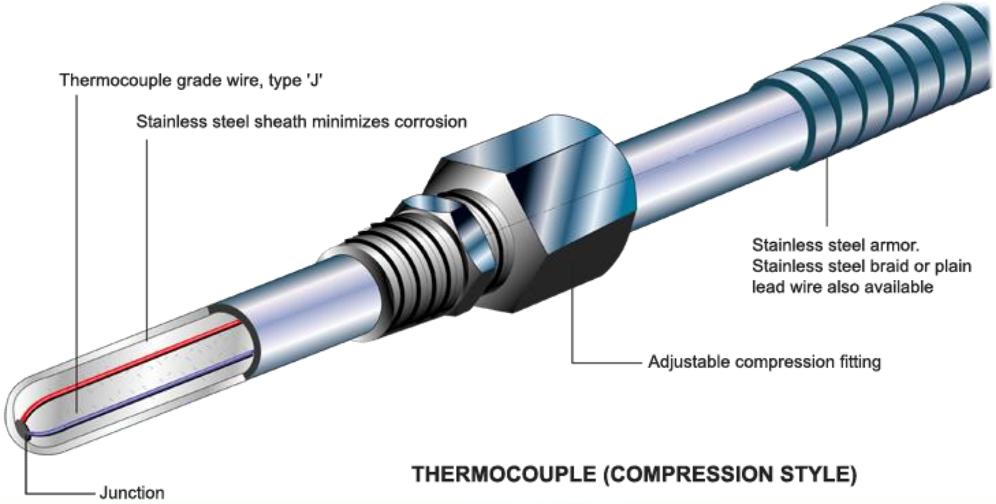
- So detector is housed in a vacuum and shielded from stray radiation.
- Source beam is chopped so signal has same frequency as the chopper.

Components of Optical Instruments

Thermal Detectors

Thermocouples

A pair of junctions formed from two pieces of metal.
Example: bismuth pressed to end of a dissimilar metal like antimony.
The two metals heat to different temperatures and a potential develops.
Responds to temperature differences of 10^{-6} K.



Components of Optical Instruments

Thermal Transducers

Bolometers

- Types of resistance thermometer made from strips of metal (i.e. Pt or Ni) or strips of semiconductor (thermistors).
- Material has large change in resistance with temperature.
- Used in specialized applications from 5 to 400 cm^{-1} (2000 to 25 μm).

Components of Optical Instruments

Detectors

For measurement in IR region

Three general types:

- Thermal
- Pyroelectric
- Photoconductivity

Components of Optical Instruments

Pyroelectric Transducers

- An electric field is applied across the material causing an electric polarization.
- The induced polarization is temperature dependent and measured by metal electrodes.

Components of Optical Instruments

A pyroelectric detector contains a piece of ferroelectric crystal material with electrodes on two sides – like a capacitor.

One of those electrodes has a black coating, which is exposed to the incident radiation.

The incident light is absorbed on the coating and causes heating of the crystal.

The crystal produces some pyroelectric voltage that can be electronically detected.

Components of Optical Instruments

Only a small group of crystals possesses a low enough crystal symmetry (e.g. monoclinic) for exhibiting ferroelectric properties and the pyroelectric effect. They have an electrical polarization which is temperature-dependent and thus leads to pyroelectric charges when the temperature changes.

Components of Optical Instruments

Triglycine sulfate (TGS, $NH_2CH_2COOH)_3 \cdot H_2SO_4$

Or modified form of that material, deuterated triglycine sulfate (DTGS).

However, TGS and DTGS are water-solvable, hygroscopic and fragile.

Components of Optical Instruments

Detectors

Pyroelectric Transducers

Made from a single crystalline wafer of pyroelectric material that is an insulator (dielectric) such as triglycine sulfate $(NH_2CH_2COOH)_3\ H_2SO_4$

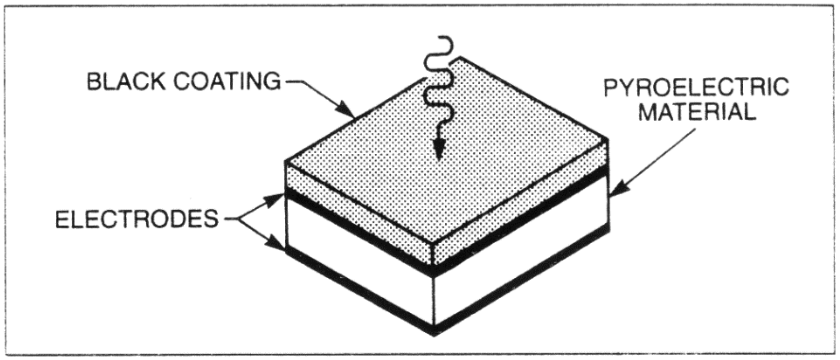


Fig. 6 Schematic of a pyroelectric detector.

Components of Optical Instruments

Detectors

For measurement in IR region

Three general types:

- **Thermal**
- **Pyroelectric**
- **Photoconductivity**

Components of Optical Instruments

Photoconducting Transducers

Thin films of a semiconducting material , i.e. lead sulfide, Hg/Cd Te, or In/Sb is deposited on a nonconducting surface and sealed in an evacuated envelope.

Components of Optical Instruments

Photoconducting Detectors

Absorption of radiation by the film promotes electrons from the valence to conducting band decreasing the electrical resistance of the semiconductor.

Lead sulfide used for near IR region (10,000 to 333 cm^{-1}). For mid and far IR use Hg/Cd Te (MCT detectors) – problem is typically need to be cooled.

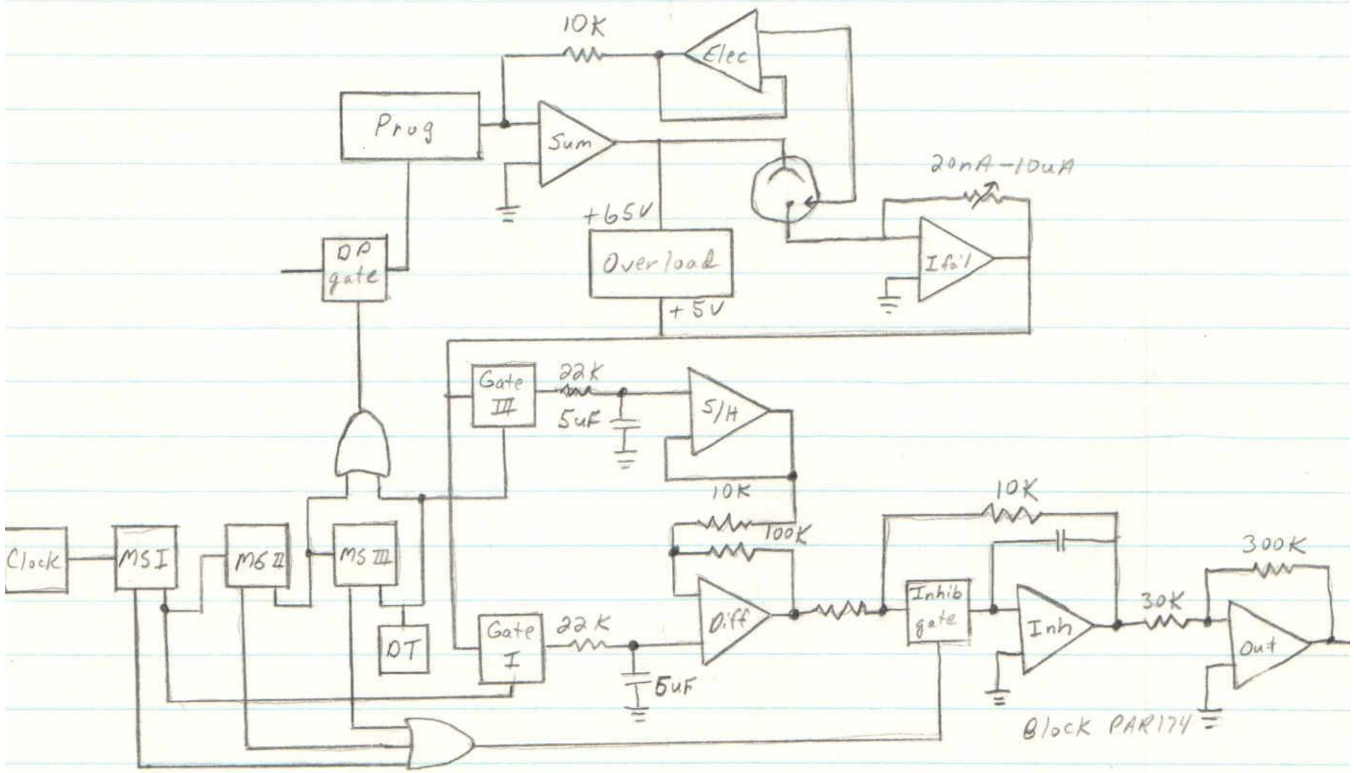
Assignment

- Read Chapters 7, 13, 15, 16, 17
- HW6 Chapter 13: 1, 2, 5-8, 12, 13, 16-19
- HW6 Chapter 13 Due 2-12 or 2-14

- Test 1- Feb 12th (Monday) – PPTs 1-7

Instrument Lab

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



Instrument Lab

II. Instrumentation

The Instrument used was a Spectrophotometer Beckman Double Beam # 1401100834. And the light source was a Beckman Hydrogen Lamp Power Supply #337997.

Schematic drawing: Figure 1: Double Beam Spectrometer

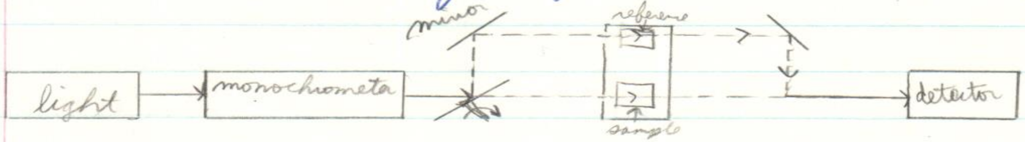


Figure 2: A scanning double-beam spectrometer with dual source, single grating.
pg. 57, Instrumental Analysis, Dean & Settle