DETECTORS

Important characteristics:

1) Wavelength response
2) Quantum response – how light is detected
3) Sensitivity
4) Frequency of response (response time)
5) Stability
6) Cost
7) convenience

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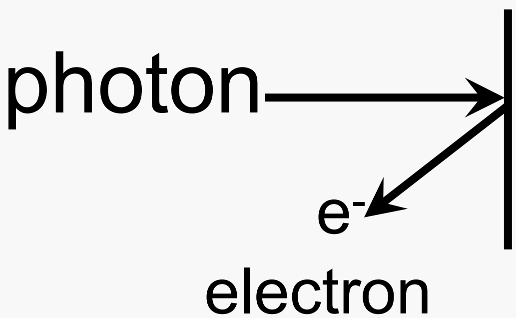
Photoelectric detectors – main detectors in visible and UV

Based on the photoelectric effect



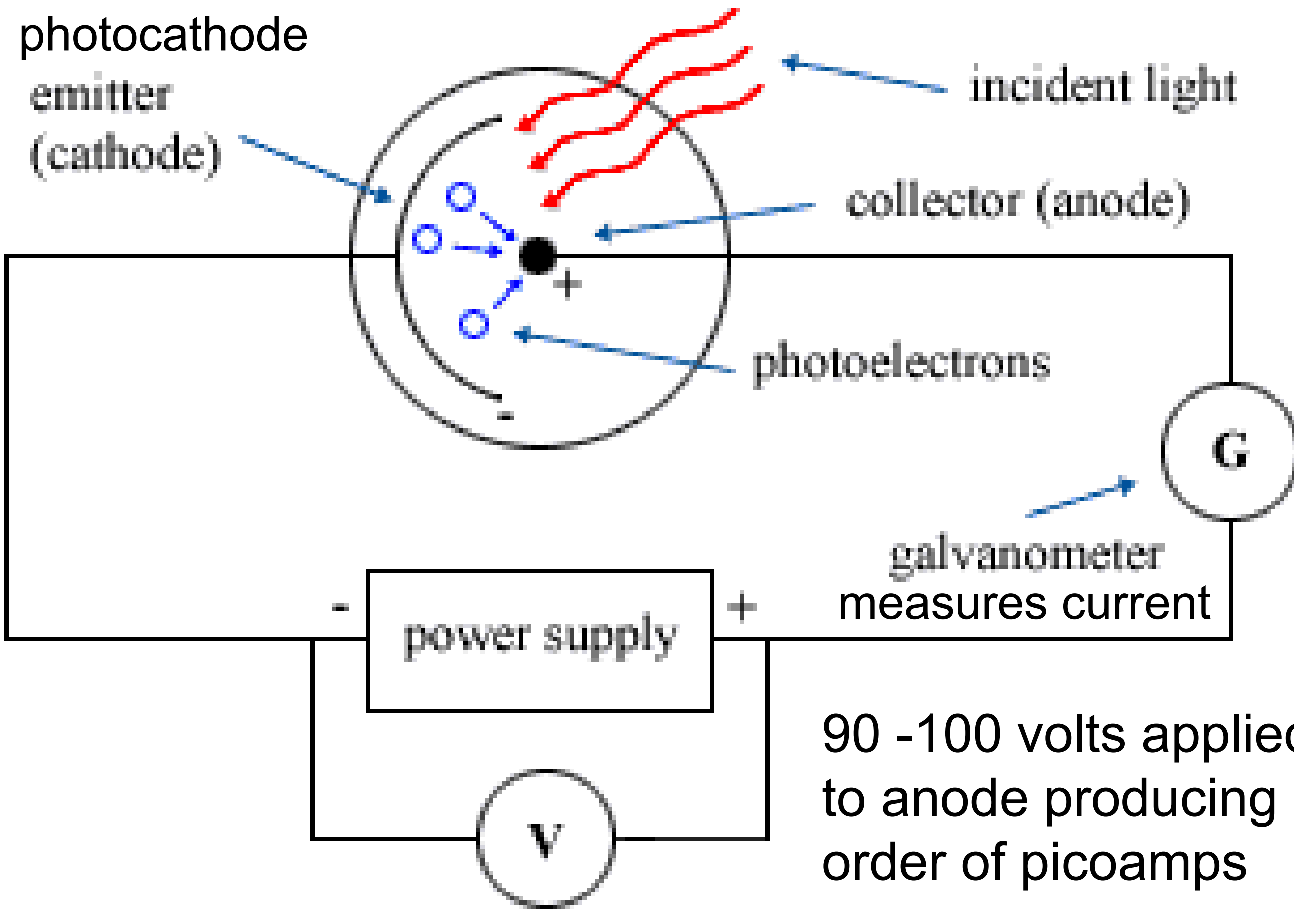
impinging radiation energy

$$E_{electron} = h\nu - w$$

energy of electron

work function of surface, lower w → easier to eject electron

Phototube or photodiode



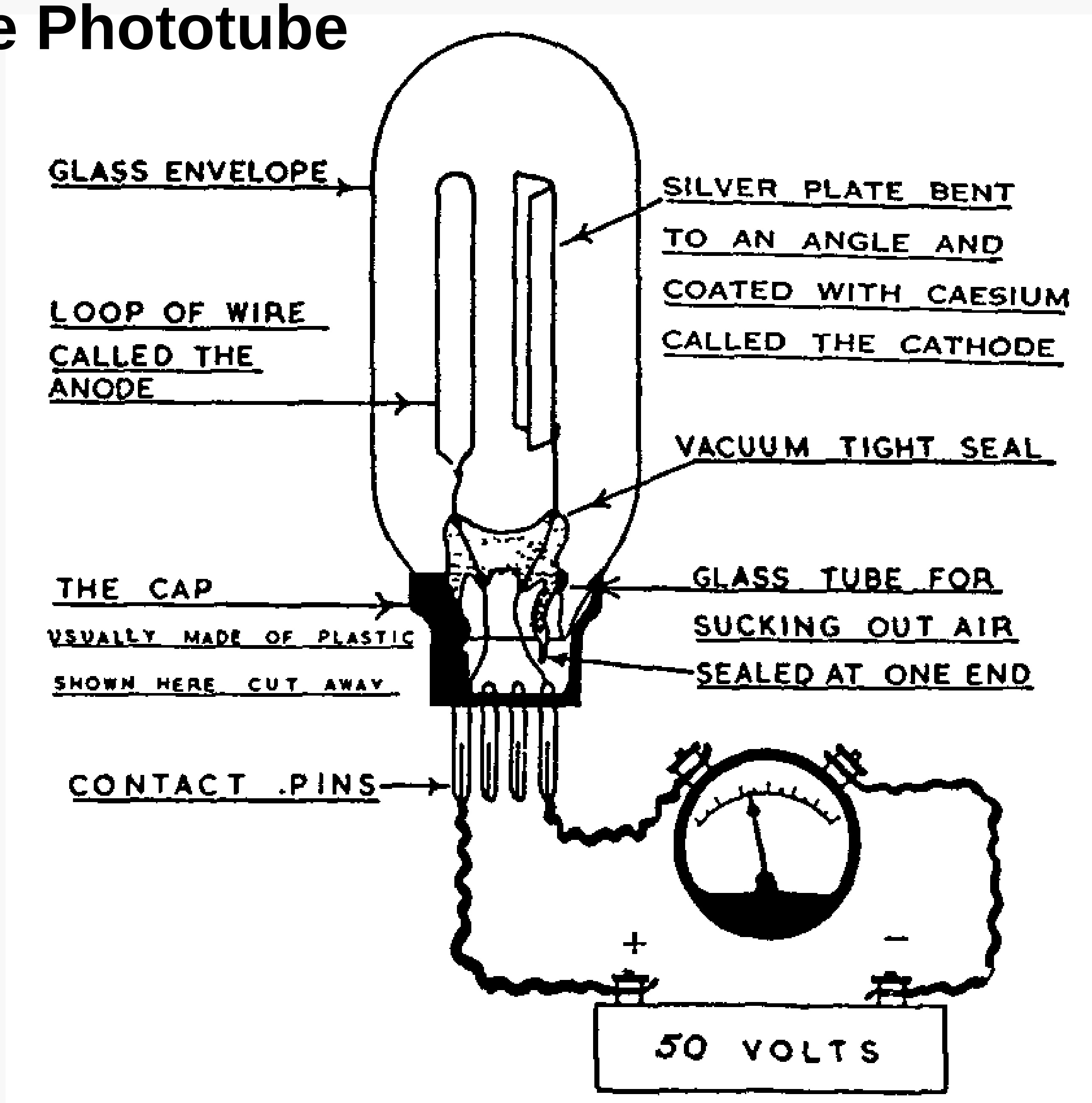
90 -100 volts applied to draw electrons to anode producing a current on the order of picoamps

Composition of photocathode determines w which in turn determines λ response

photons → electrons → current

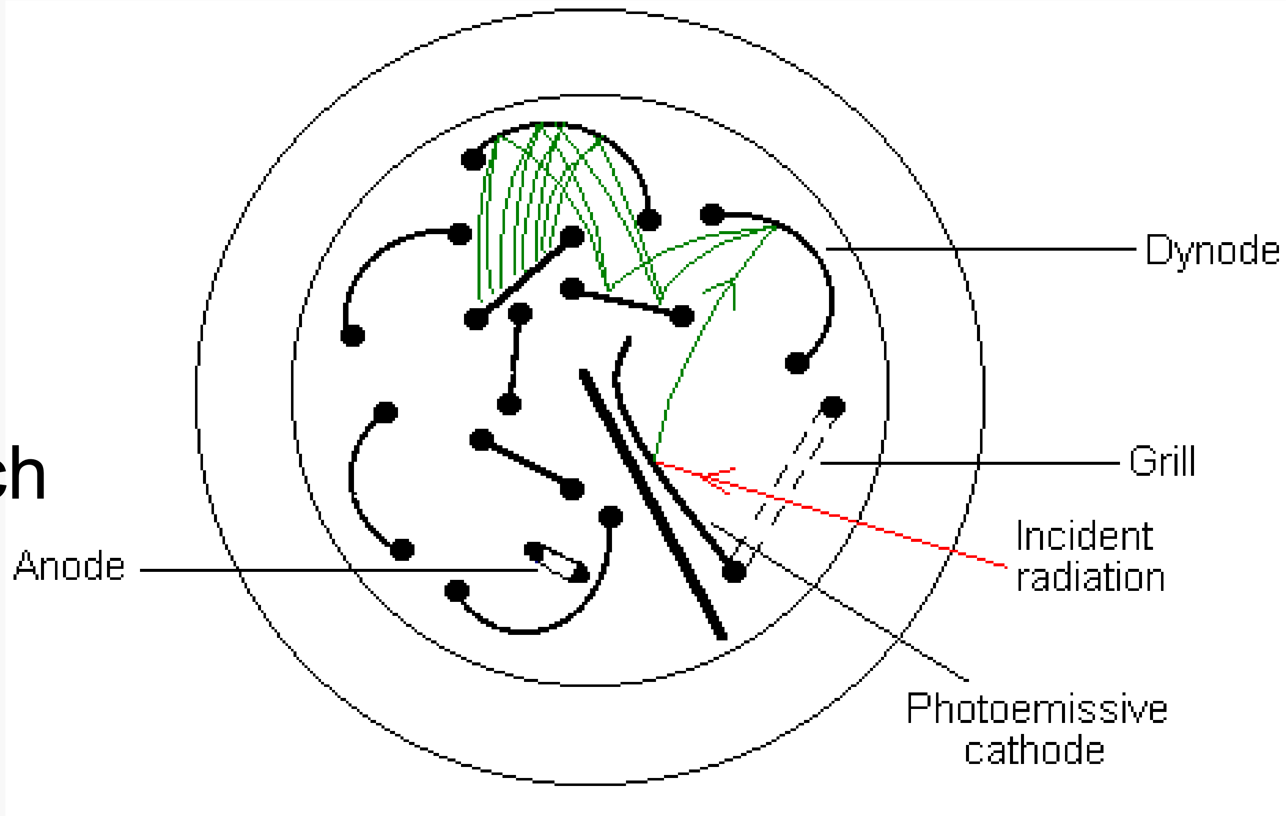
Usually need current to voltage converter to display signal as voltage proportional to # of photons

Primitive Phototube



Photomultiplier Tube or multiplier phototube (PMT) → essentially a phototube with built in amplifier

90 – 100 volts between photocathode & 1st dynode & between each successive dynode



1 photon → bunch of electrons

Each dynode increases the number of electrons

Typically 10-20 dynodes

Photomultiplier Tubes (PMTs)

Standard PMT
Normal device for
UV-Vis absorption

End-On PMT
Typically used where required by
space or geometry constraints

Characteristic Parameters of PMTs:

(typically specified by manufacturers)

a) Quantum efficiency = **f**(λ)

$$= \frac{\text{photoelectrons ejected}}{\text{photons striking photocathode}}$$

b) Cathode sensitivity = μA/lumen or μA/watt

have to specify λ and use a standard source at known temperature

c) Gain = $f\,(g\,\delta)^n$

- n: number of dynodes
- f: collector efficiency
- g: transfer efficiency dynode to dynode
- δ: $\frac{\text{\# of electrons emitted}}{\text{electron striking dynode}}$

Typical gain 10^6 electrons/photon in

$g\,\delta = 4.5$

d) Spectral response – depends on photocathode work function (sensitivity as a function of wavelength) *Very Important*- must be corrected for when scanning e.g. in fluorescence spectrum

e) Dark current – current when photomultiplier is operated in complete darkness. Lower limit to the current that can be measured → dark current needs to be minimized if low intensities are to be measured

Thermionic emission is an important source of dark current → this thermal dark current is temperature dependent

Therefore, cooling the photomultiplier tube reduces dark current (-40 oC is sufficient to eliminate the thermal component of dark current for most photocathodes

Smaller w → higher dark current (smaller w's are associated with photocathodes that respond at longer λ's i.e. red sensitive cathodes) → low energy photons

If photocathode is exposed to bright daylight without power, it traps energy and it takes 24 – 48 hrs in the dark with high voltage on in order for dark current to go back to equilibrium value

Long term exposures to bright light leads to sensitivity loss particularly at longer λ

Noise – due to random fluctuations in:

1) Electron current (shot noise)
2) Thermal motion of conducting electrons in the load resistor (Johnson noise)
3) Incident photon flux (quantum noise) – flux of photons varies statistically

Shot noise

$$i_{noise} = (2\ e\ i\ \Delta f)^{½}$$

signal current

bandwidth of detection system

noise current

charge on electron

Shot noise is proportional to the square root of the signal

Except at very low currents, shot noise predominates

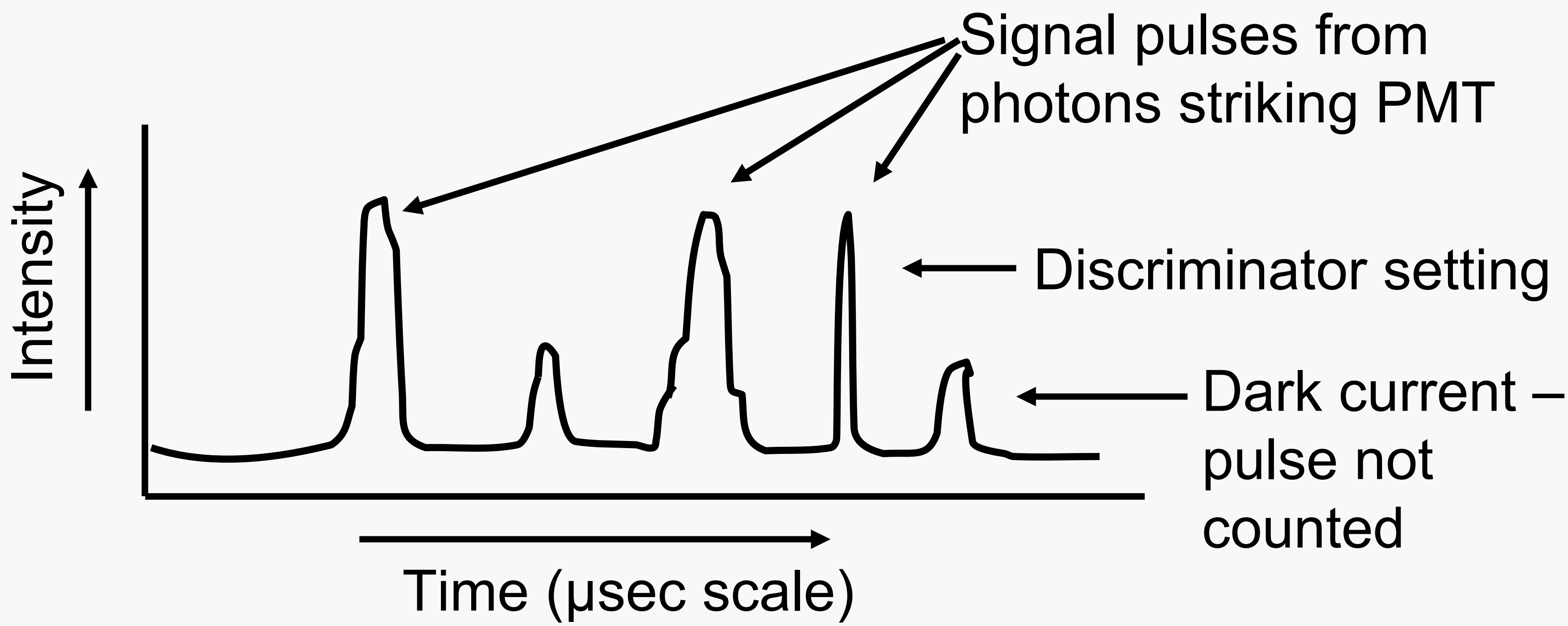
Advantages of PMTs

1) Stable except after exposure to high light levels
2) Sensitive
3) Linear over several orders of magnitude
4) Reasonable cost
   1) Simple PMT for visible region = $100
   2) Quartz jacketed PMT for UV & red sensitive tubes for near IR can be more expensive
5) Long lifetime
6) Rapid response (on the order of nanoseconds)

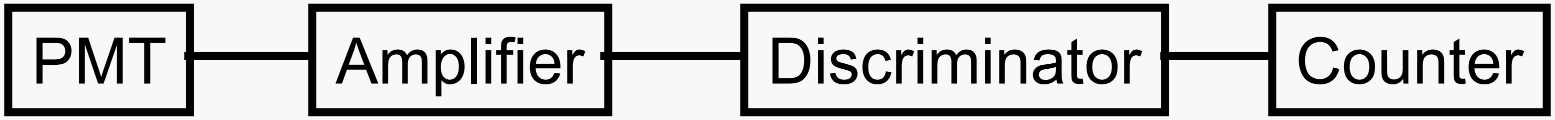
IR detectors not nearly as good as PMTs

Normally measure DC level of current resulting from all electrons generated in PMT. However, at low light levels it is possible to do **photon counting**

Each photon gives rise to a pulse of electrons



Block Diagram of Photon Counting System

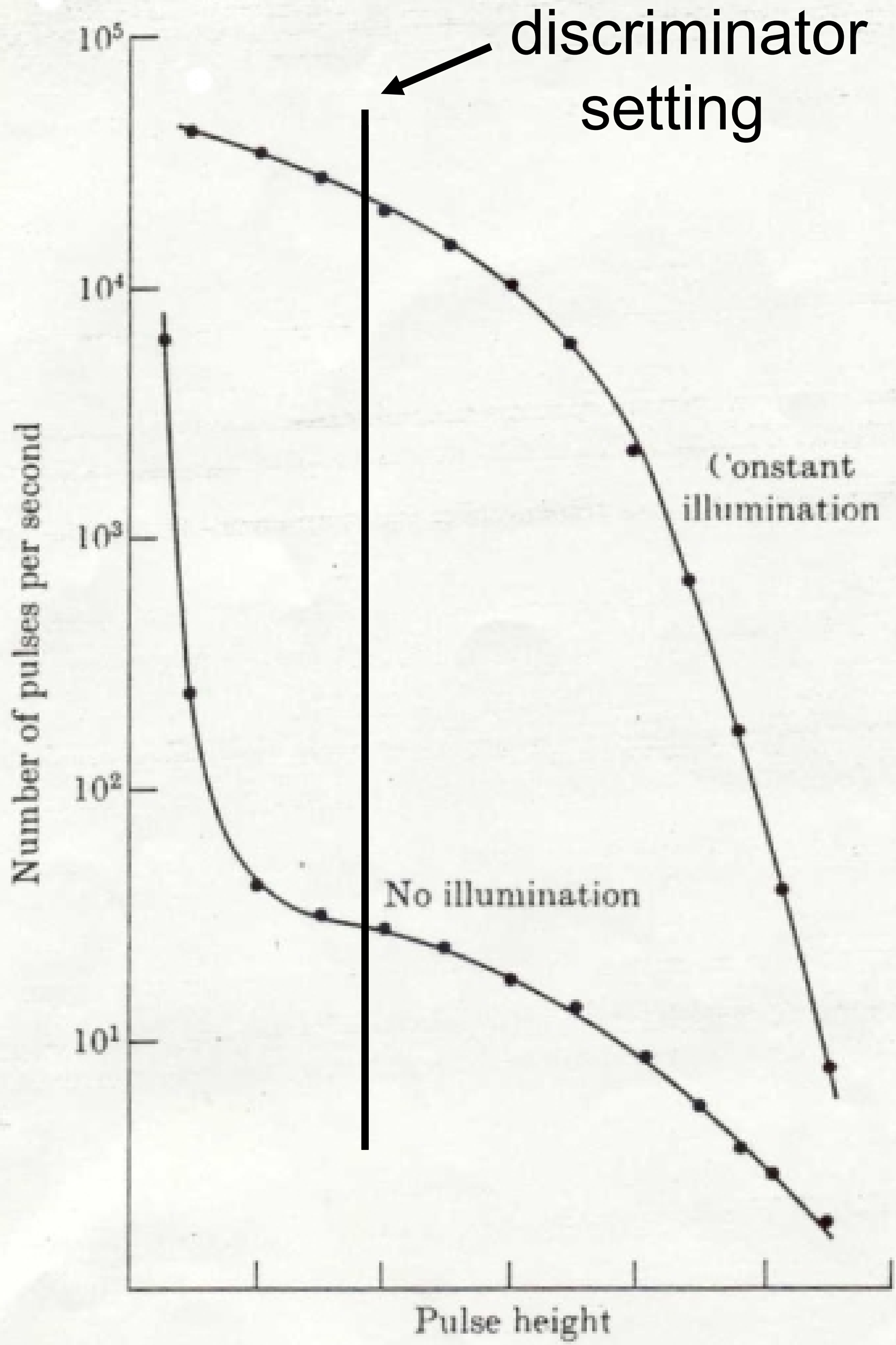


Discriminator sets the level for counting.

Pulses exceeding the discriminator level are counted. Pulses below the discriminator level are not counted.

Dead Time – after each pulse, electronics need some time to recover = dead time. Any pulse arriving during the dead time interval will not be counted (typically 0.11 to 0.01 μsec)

Dead Time Loss – decrease in signal because of uncounted pulses arriving during the dead time. This becomes significant at count rates somewhere between 10^5 & 10^6 counts/sec = upper limit to intensities measured by photon counting

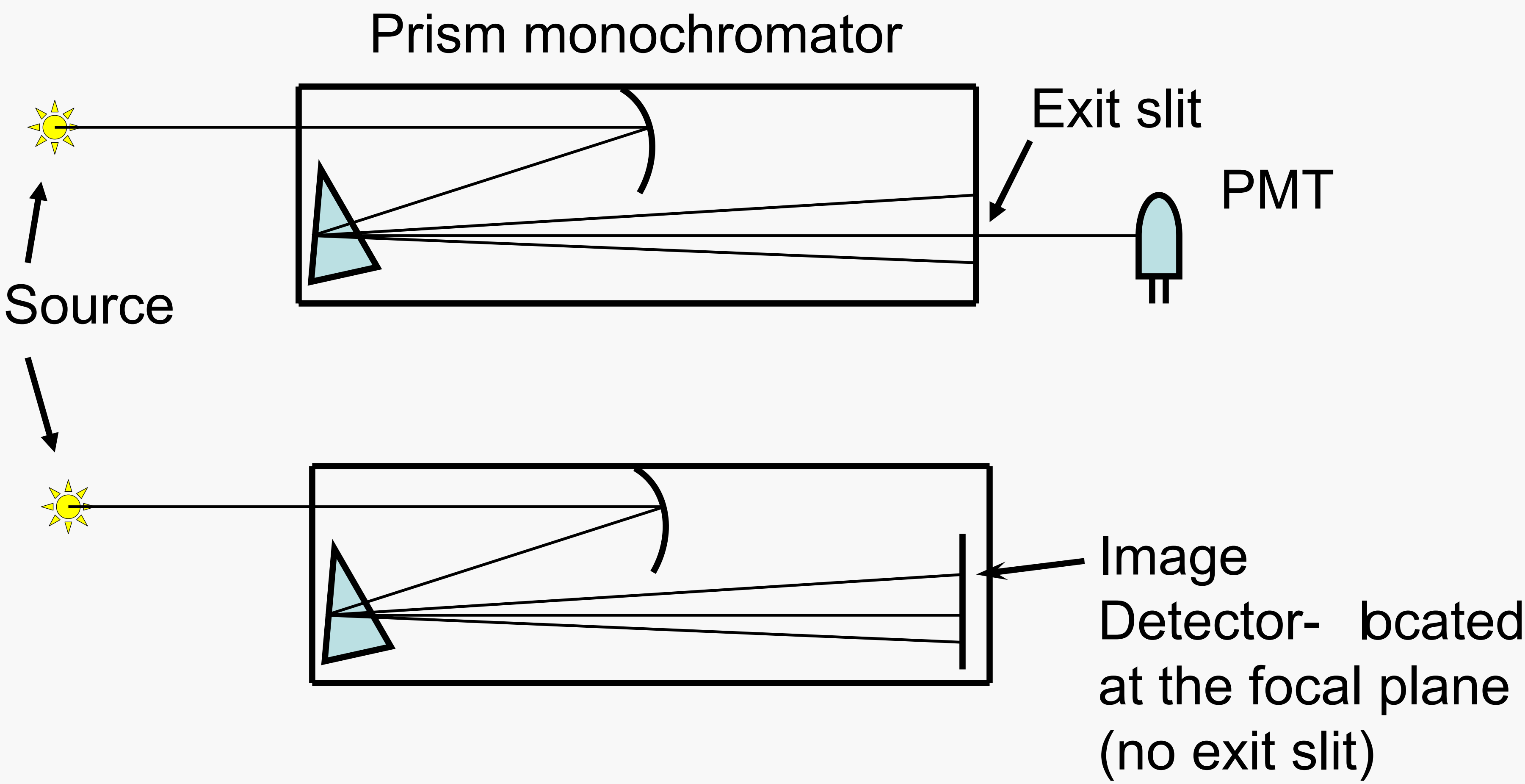


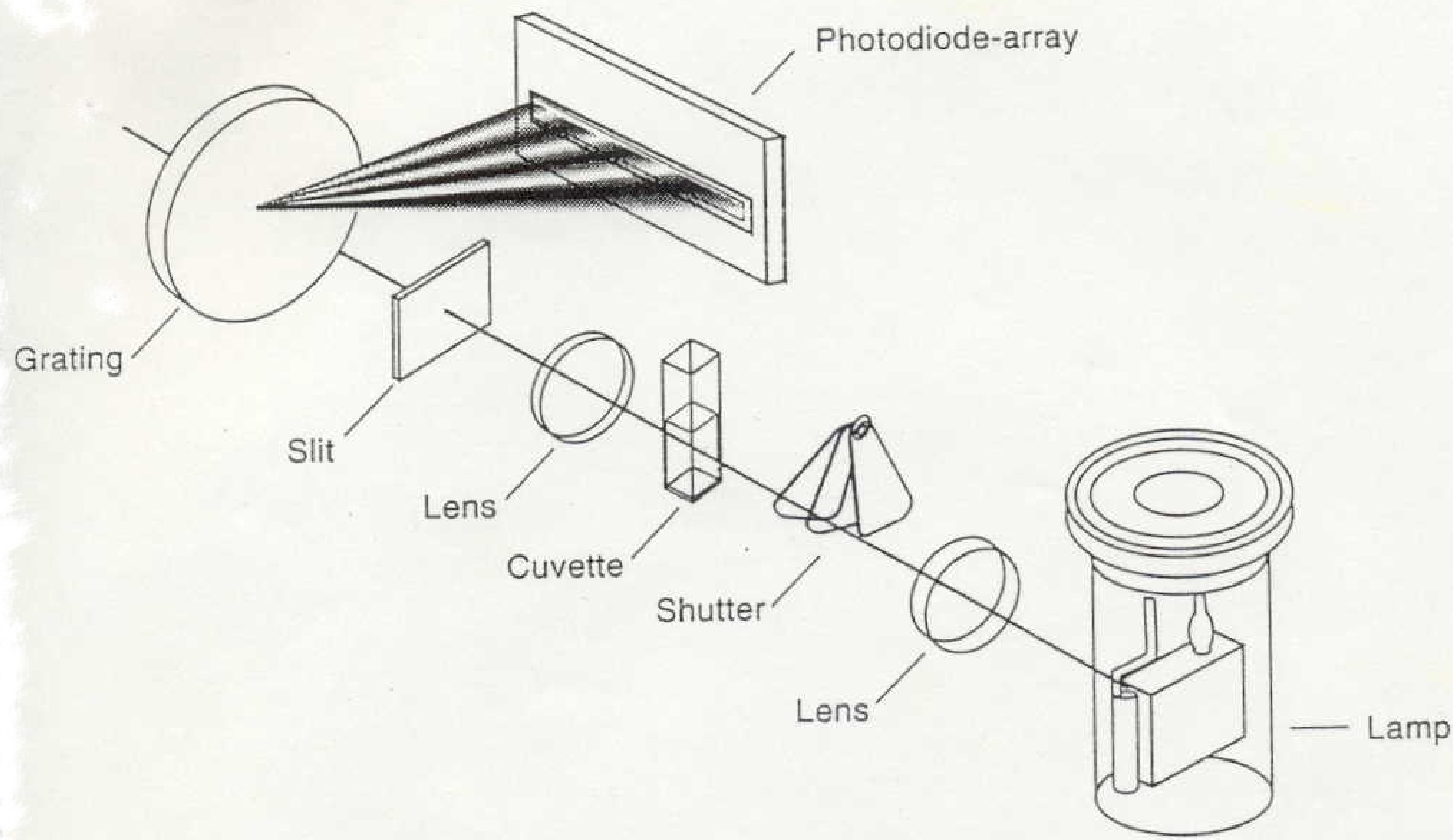
Plot of number of photon counting pulses observed vs pulse heights for 2 conditions, constant light (top) & no light (lower)

If discriminator is set too high → get too few pulses counted (see upper curve)

If set too low → get too many pulses counted (lower curve)

Image Detectors – powerful detectors used instead of PMTs to detect a complete spectrum or part of a spectrum




Photodiode-array
Grating
Slit
Lens
Cuvette
Shutter
Lens
Lamp

Common Image Detectors

1) Electron Image Intensifiers
2) Image Dissectors
3) Solid-State Imaging Systems
    a) Vidicon tubes
    b) Optical Multichannel Analyzers (OMAs)
    c) Photo Diode Arrays (PDAs)
4) Charge Coupled Devices (CCDs)

These are often used with intensifiers – device to increase sensitivity

Photodiodes, Linear Diode Array & Two Dimensional Arrays

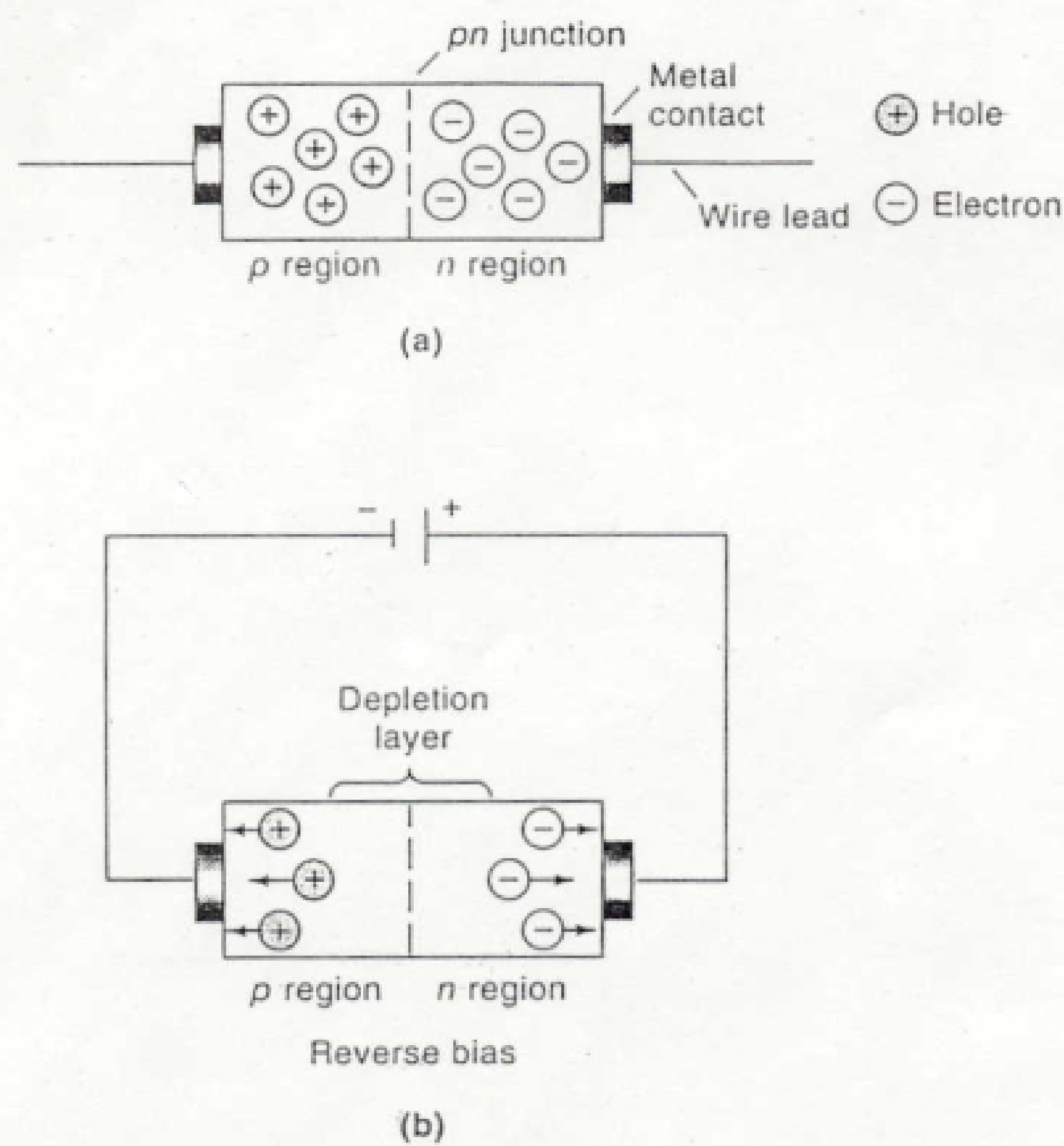
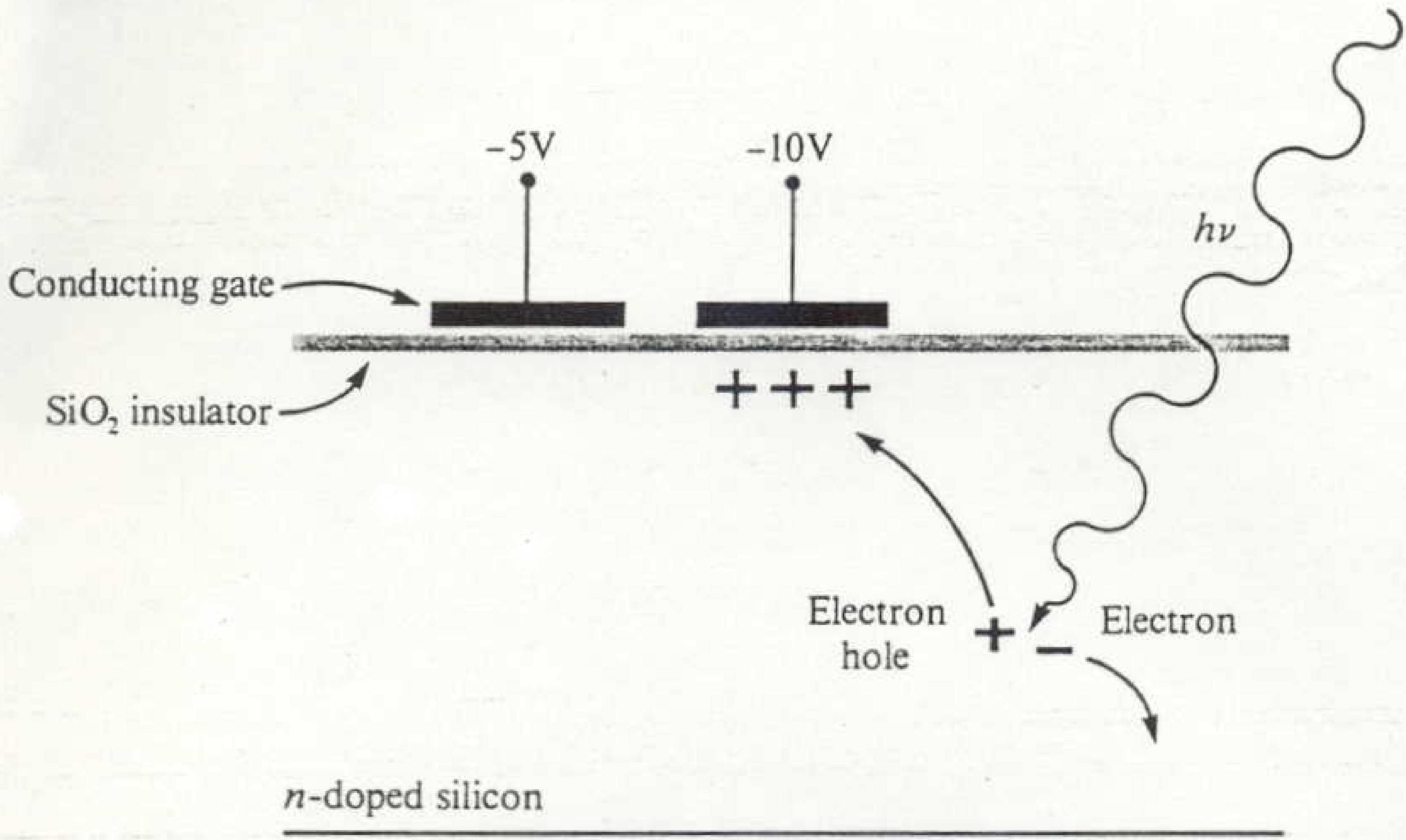
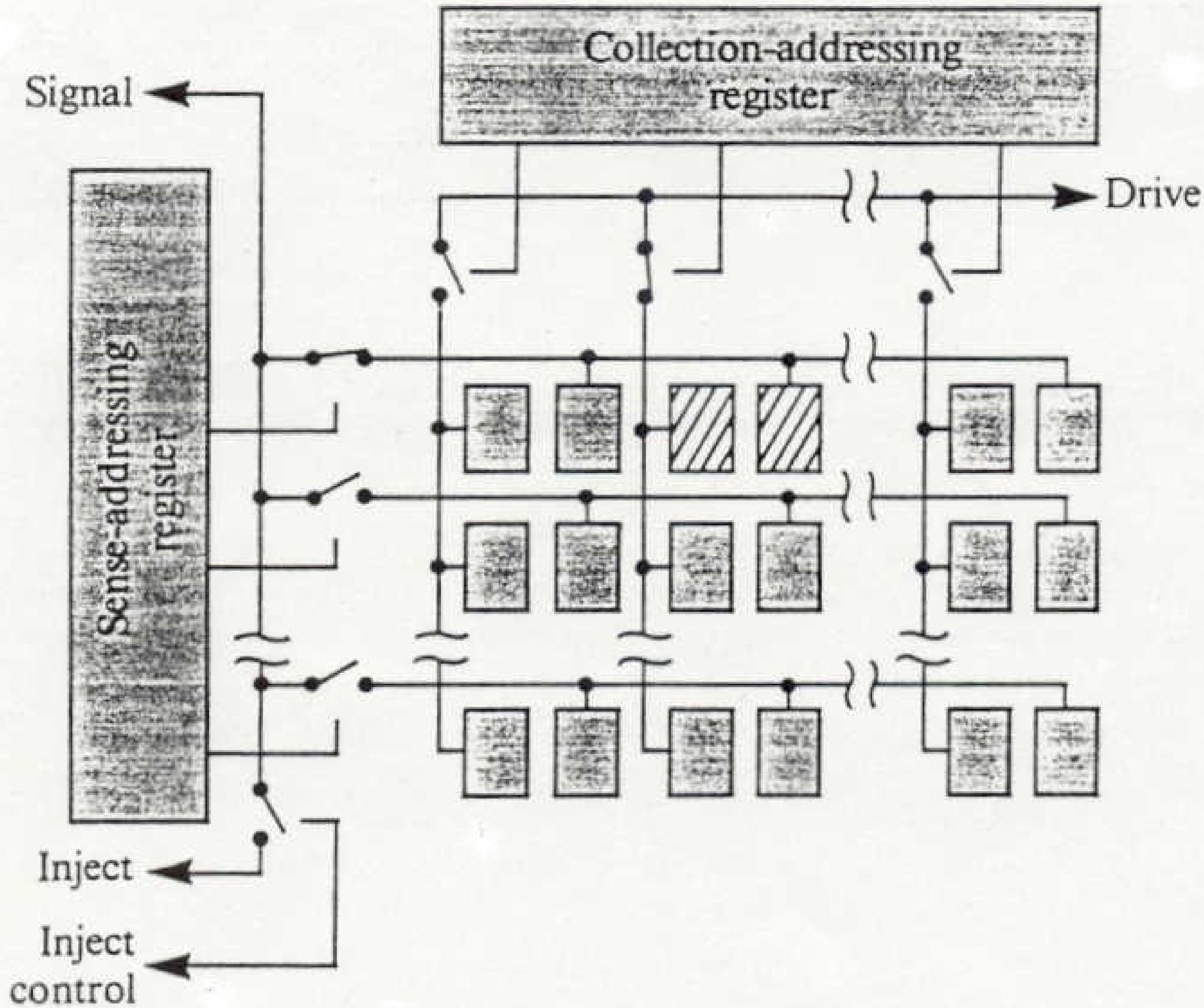


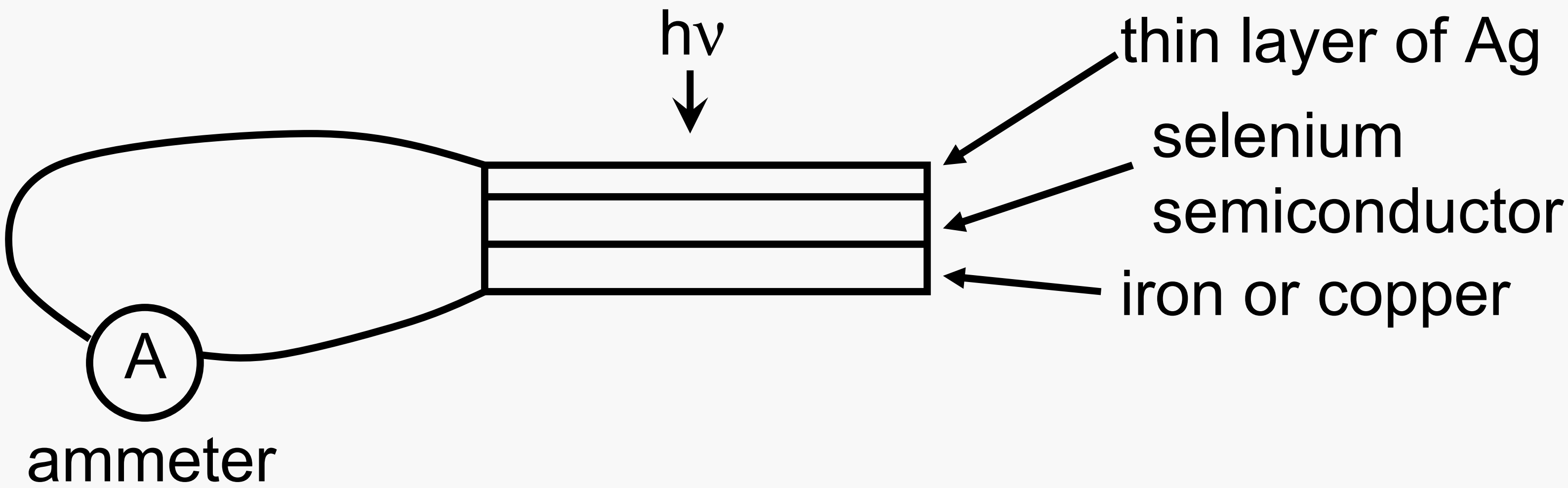
FIGURE 6–24 (a) Schematic of a silicon diode. (b) Formation of depletion layer, which prevents flow of electricity under reverse bias.

Charge Coupled Device (CCD)




Collection-addressing register
Signal
Drive
Sense-addressing register
Inject
Inject control

Photovoltaic Cell

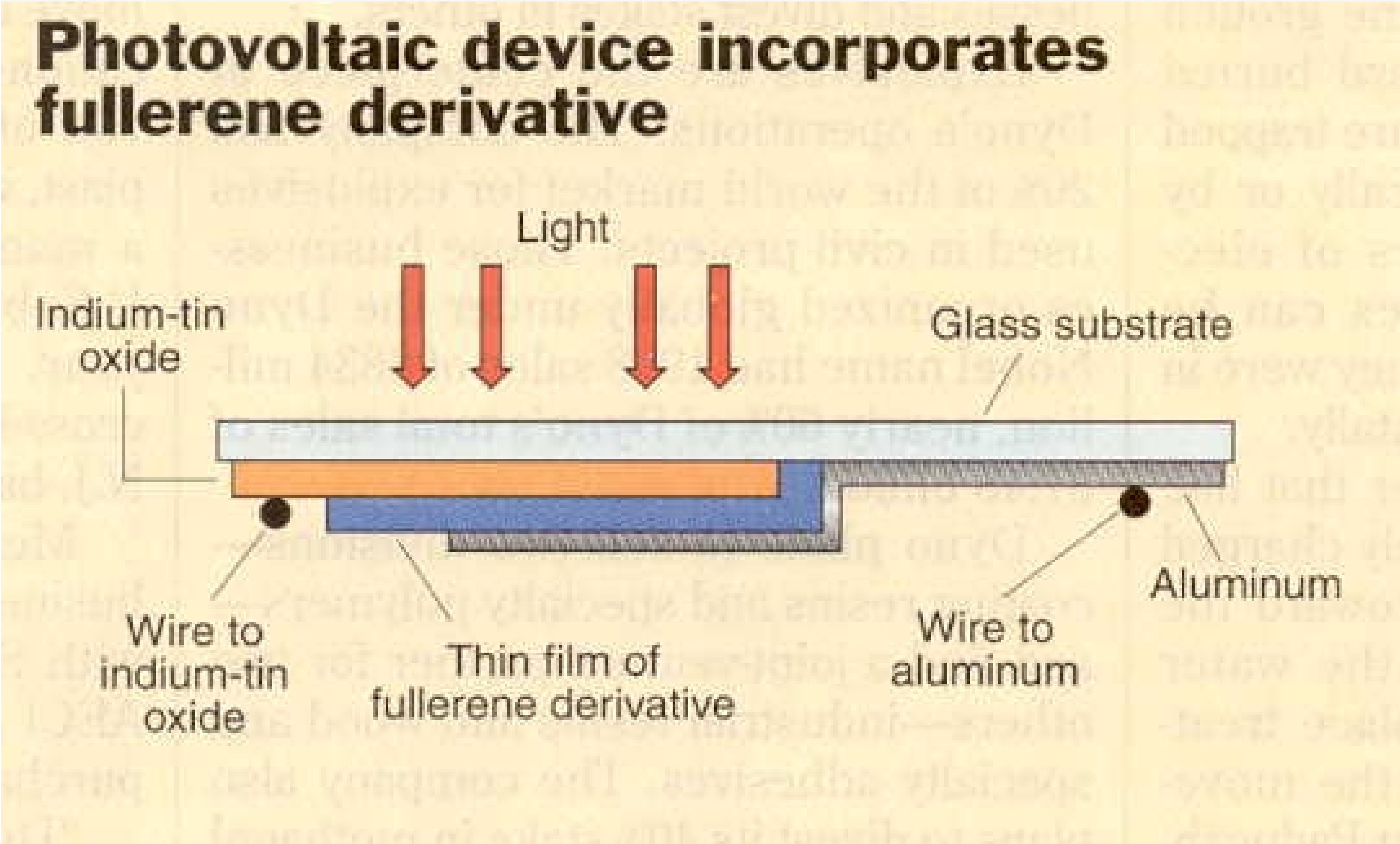


Light excites electrons in Se at Se-Ag interface into "conduction band" and to metal conductor → current

Good only for high light levels

Subject to fatigue effects

Another example of a Photovoltaic cell



Photoconductive detector – semiconductor used with voltage applied across it

Photons → electrons promoted to conduction band → high conductivity (lower resistance)

PbS, PbSe, InSb good for 0.7 to 4.5 μm (near IR)

Ge activated with Cu, Au or Zn good from 2 to 15 μm – operated at ~5 ^{o}K

Considerably less sensitive than PMTs

Better than thermal detectors in IR

Photographic detection – place film at focal plane and expose (integrating detector)

Advantages:

1) good resolution
2) fairly sensitive
3) covers entire spectral region

Disadvantages:

1) very old technique
2) quantitatively very bad (can use densitometer)

Thermal Detectors for IR – in IR region photons have lower energies → necessary to resort to <u>thermal detectors</u> – radiation absorbed and temperature change is detected

Response time is limited by rate of heat transfer → slow

Sensitivity is also much poorer

Three types of thermal detectors:

1) Thermocouples (most common) – junction between dissimilar metals often covered with black substance to increase absorption

Voltage difference across junction is a function of temperature

Amplify signal and detect

Response time ~60 msec (i.e. slow)

Sensitivity is greater using a thermopile = a bundle of many thermocouples

2) Bolometer (thermistor) – resistance is a function of temperature

Different kinds → Ni or Pt metal or oxides like NiO, CoO or MnO

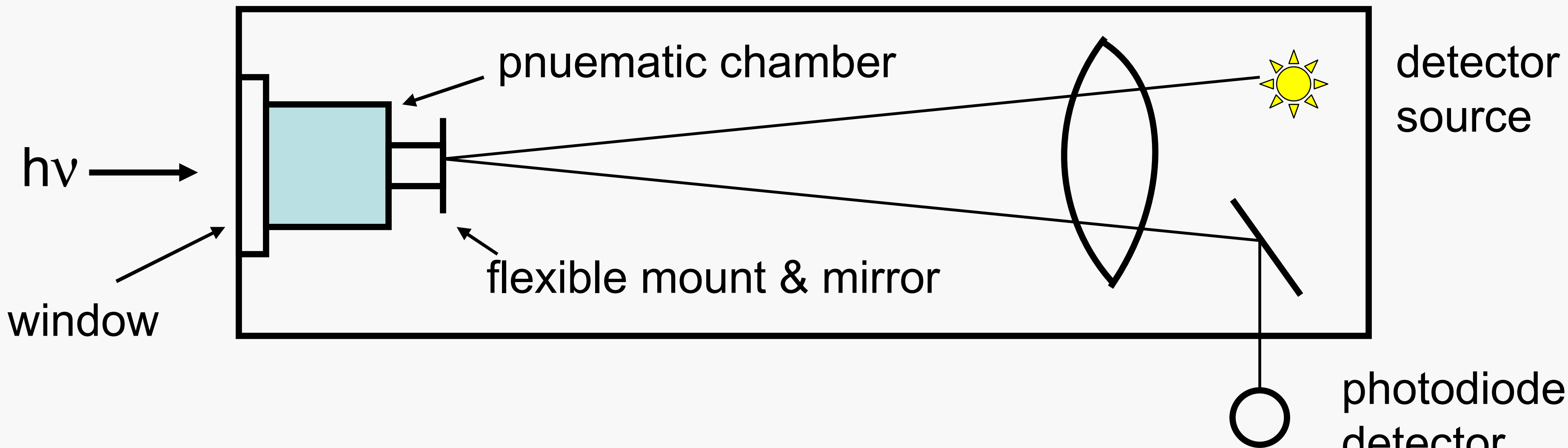
Many have black coating on side toward source and a heat shield around them

Typically connected to a bridge circuit

Johnson noise is important

Requires stable power supply

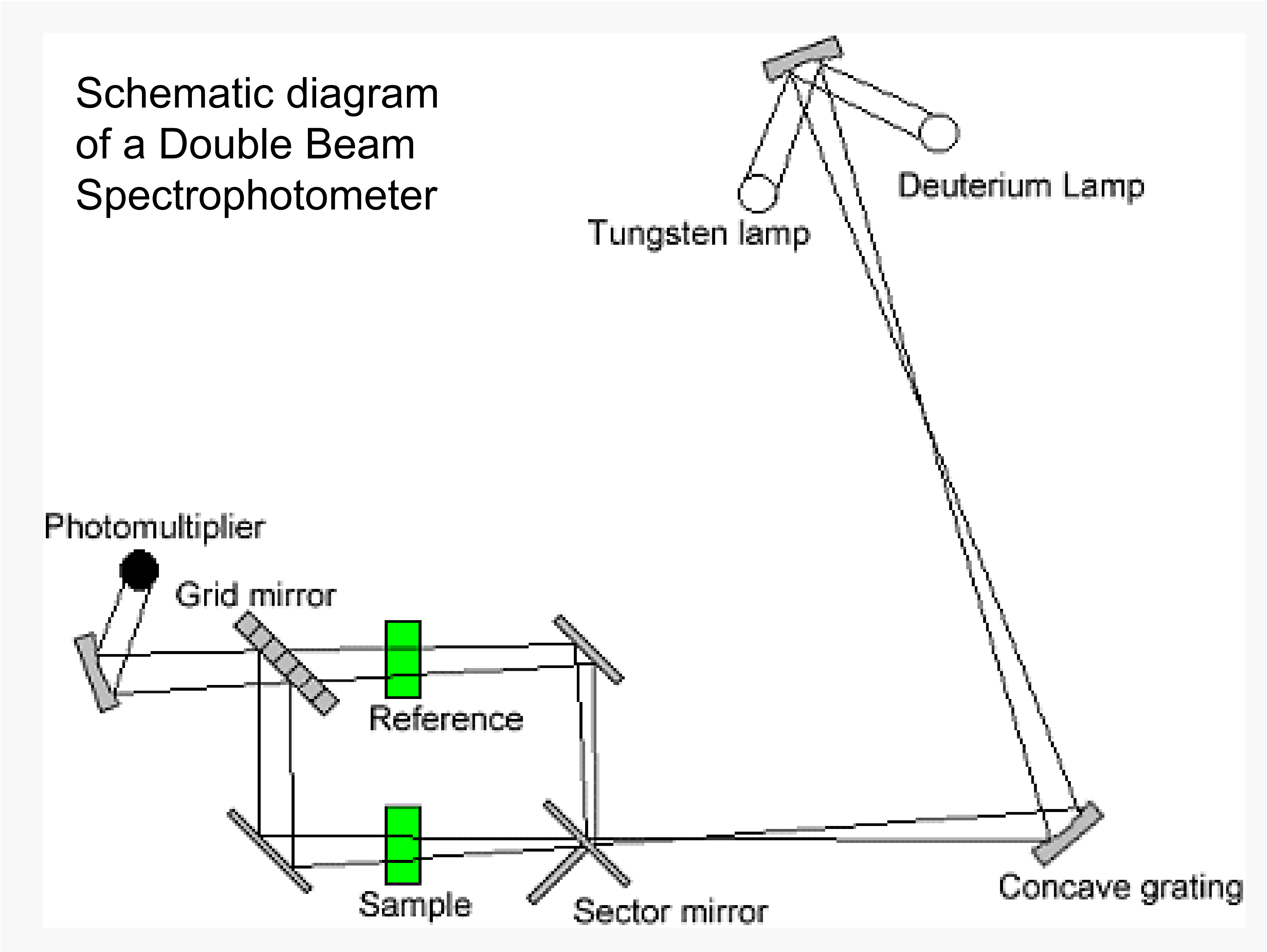
3) Golay Pneumatic Detector (best performance characteristics)



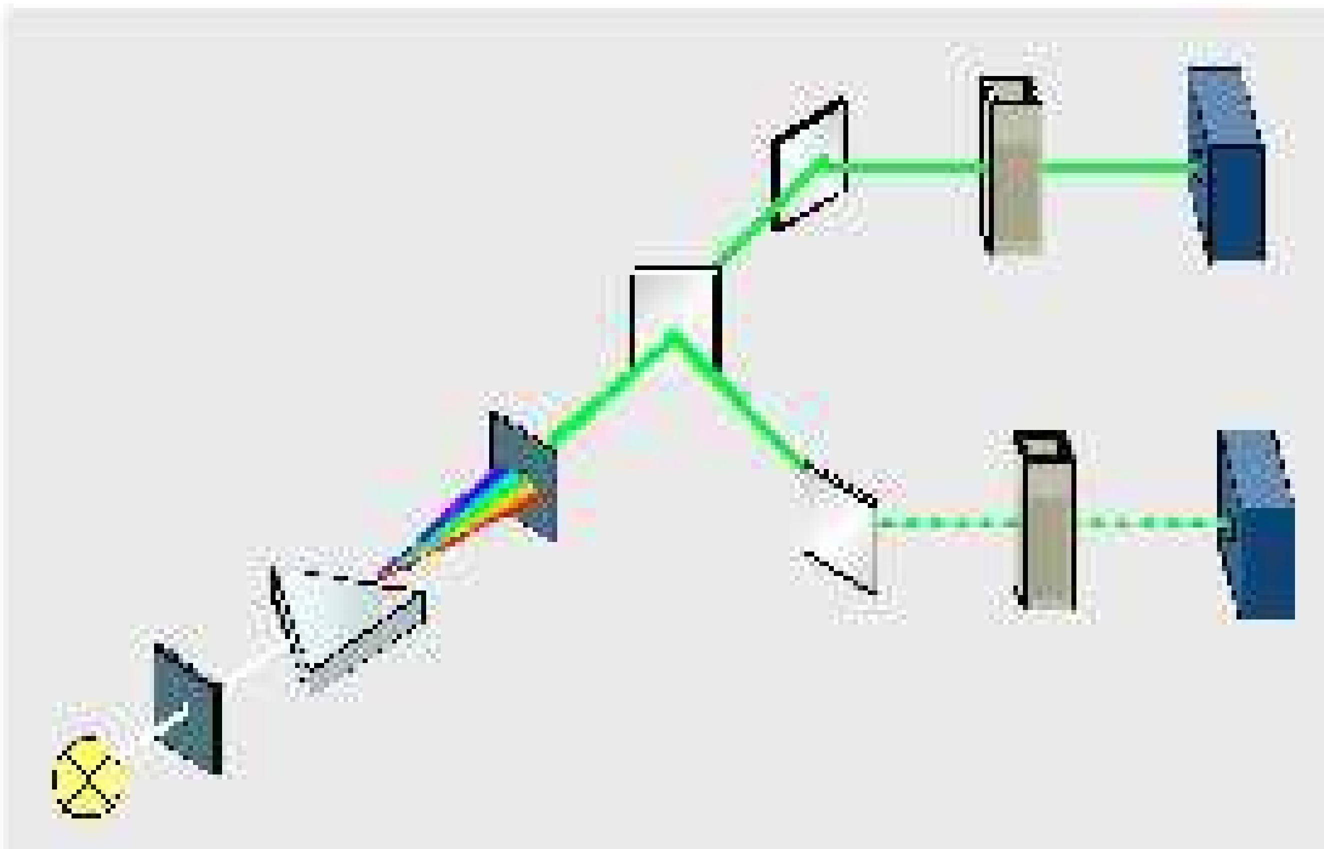
Heat from radiation → gas expands →
mirror position changes → amount of light reflected to photodiode changes

Best sensitivity

Response time ~4 msec → heat transfer in gas phase faster than in solid


Schematic diagram
of a Double Beam
Spectrophotometer
Deuterium Lamp
Tungsten lamp
Photomultiplier
Grid mirror
Reference
Sample
Sector mirror
Concave grating

Schematic diagram of a Double Beam Spectrophotometer



Schematic diagram of a Single Beam Spectrophotometer