chem 5390

Advanced X-ray Analysis

LECTURE 8

Dr. Teresa D. Golden
University of North Texas
Department of Chemistry

Instrumentation

B. Detectors

Properties of Detectors

-quantum counting efficiency

-linearity

-energy proportionality

-resolution

Instrumentation

B. Detectors

Quantum counting efficiency – efficiency of the detector in collecting radiation. Ideal efficiency, $I \sim I_o$, for characteristic photons.

Instrumentation

B. Detectors

Linearity – detector range

Dead time (τ) – time required for the detector to collect a photon, convert it to a pulse, and count the pulse.

R – count rate or pulse rate (pulse/s)

When photon flux (I/s) is equal to count rate (pulse/s) there is no dead time. However the measured count rate, R_m, will always be lower than the true count rate, R_t.

$$R_t = R_m/(1-R_m\tau)$$

Instrumentation

B. Detectors

Two types of dead time

<u>paralyzable (nonextending)</u> – complete saturation of the detector, causing detector to stop working. (usually over 100,000 counts/s)

<u>nonparalyzable (extending)</u> – increasing loss in counts with increasing count rate, but does not saturate.

Instrumentation

B. Detectors

Energy proportionality – when the size of the output pulse, V, is proportional to the energy, E, of the incident x-ray photon.

Instrumentation

B. Detectors

Resolution – measure of detectors ability to resolve two x-ray photons of differing energy.

Kα and Kβ energies of copper, are at 8.041 and 8.904 keV, respectively.

Kα1=8.047 keV and Kα2=8.027 keV.

Instrumentation

B. Detectors

Point detectors (0-D)	Linear detectors (1-D)	Area detectors (2-D)
Scintillation detector (NaI, YAP)	Gas proportional counter	Multi-wire proportional counter
Gas proportional counter	Gas detector	CCD-camera
Si(Li) solid state detector	Linear CCD	Image plate detector (IP)
Ge solid state detector	Micro-strip silicon detector	Photographic film
Silicon pin diode	Image plate detector (IP)	
Silicon drift detector	Photographic film	
Ionization chamber		

Instrumentation

B. Detectors

	Scintillation detector	Gas PSD	Photographic film	MWPC	CCD
Active area	n.a.	0	++	+	+
Spatial resolution	++	+	++	+	++
Energy resolution	0	+	––	+	––
Real time photon counting	++	++	––	++	––
Back ground noise	0	++	––	++	0

Instrumentation

B. Detectors

Table 5.3. Properties of Common X-ray Detectors

	Scintillation			Xe Sealed Gas			Si(Li)		
Property	Cr	Cu	Mo	Cr	Cu	Mo	Cr	Cu	Mo
Quantum efficiency (%)	60	98	100	90	90	75	90	95	80
Linearity—loss at 40,000 c/s	Less than 1%			Up to 5%			Up to 50%		
Proportionality	Very stable			Pulse shift at high c/s			Pileup, etc., at moderate c/s		
Resolution (%)	55	45	31	17	14	10	3	2	1

Instrumentation

B. Detectors

Majority of detectors depend on x-rays to ionize atoms (either as a gas or on a solid)

Types of detectors:

Proportional

Geiger

Scintillation

Solid State (Semiconductor)

(Photographic Film)

Instrumentation

B. Detectors

1. Proportional Detector

Common detector

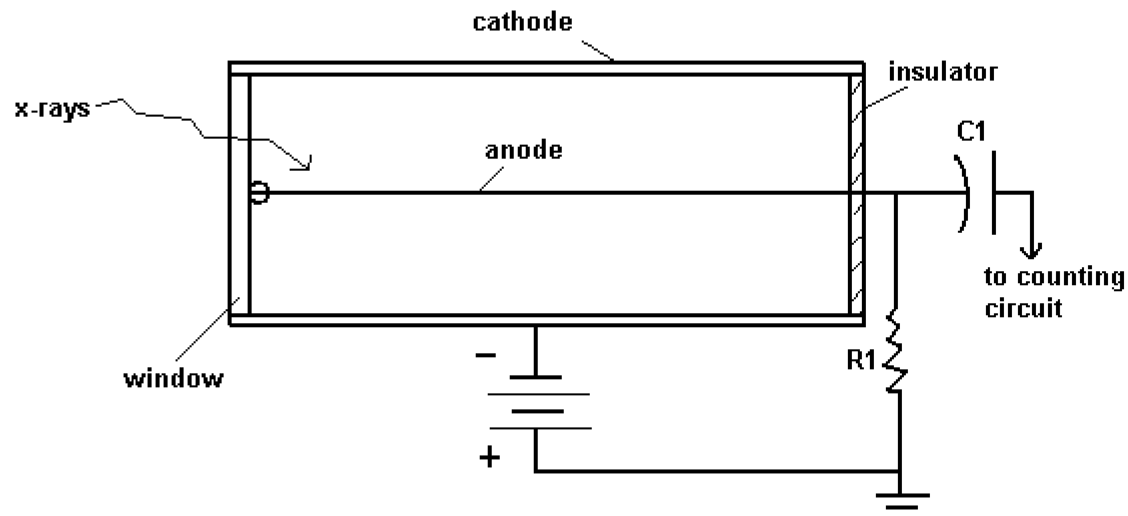
A metal tube (cathode) filled with a gas (i.e. Ar, Xe, or Kr) and contains a thin metal wire (anode) running down the center.

There is a constant potential difference between the cathode and anode.

Instrumentation

B. Detectors

1. Proportional Detector



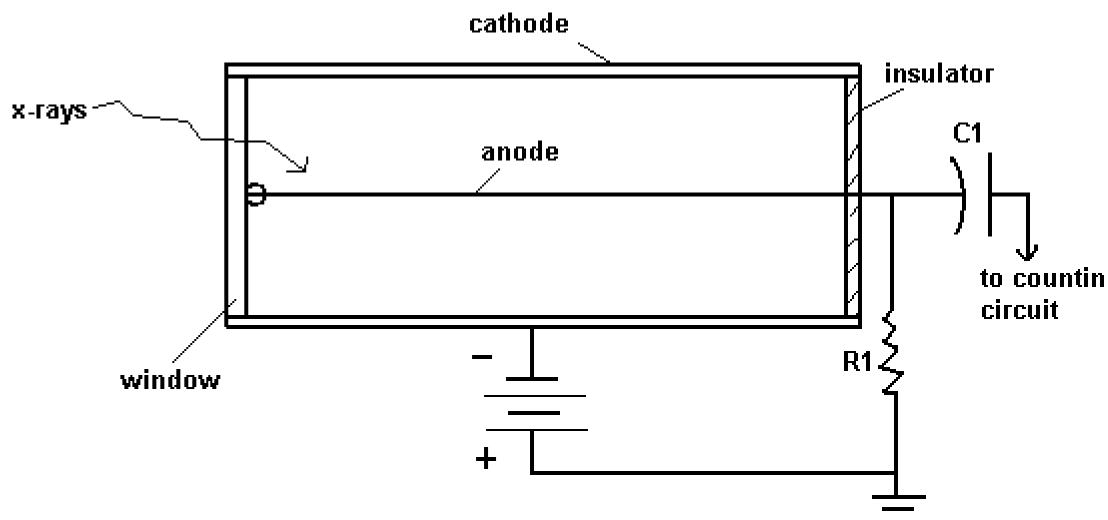
-X-rays enter the tube through a transparent window and are absorbed by a gas – typically Xe

-The gas ejects a photoelectron and becomes ionize (an ion/electron pair of an electron and positive ion is produced)

Instrumentation

B. Detectors

1. Proportional Detector



-Ionized gas (+) moves toward the cathode (-)

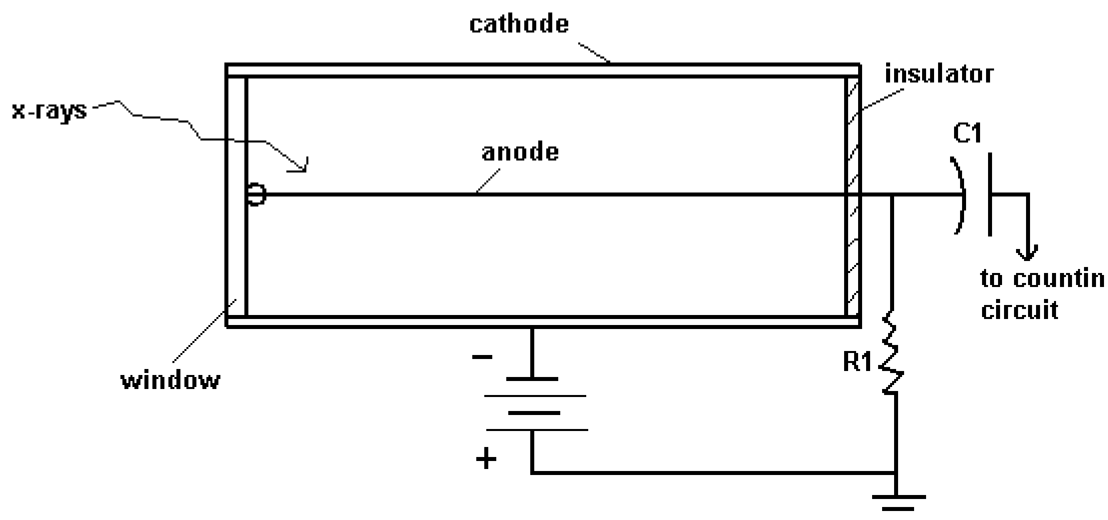
-Electrons (-) move toward the anode (+)

-A small current is measured and related to the x-ray intensity.

Instrumentation

B. Detectors

1. Proportional Detector



The ionization energy of the noble gas is ~20 - 30eV
For one Cu x-ray photon, the energy is 8.04 KeV
So ~270 electron-ion pairs are produced with CuKα

Instrumentation

B. Detectors

1. Proportional Detector

If the voltage difference (ΔV) between the cathode and anode is ~1000V, then one photon can cause multiple ionization or "gas amplification".

Instrumentation

B. Detectors

1. Proportional Detector

Gas amplification - electrons are produced by the primary ionization event

These electrons are accelerated (by the voltage) towards the anode.

The electrons gain energy and ionize other gas atoms in the path (secondary ionization)

This avalanche of electrons hits the wire (anode) and cause a pulse of current

The current is discharged into a ratemeter at the capacitor, C1.

Instrumentation

B. Detectors

1b. Position-sensitive detectors (PSDs)

Essentially a gas proportional detector in which electron collection and pulse-generating electronics are attached at both ends of the anode wire.

The anode wire is made poorly conducting to slow down the passage of electrons. Measure the rate at which the pulse develops (rise time) at each end of the wire and can correlate rise time to position on anode wire.

Instrumentation

B. Detectors

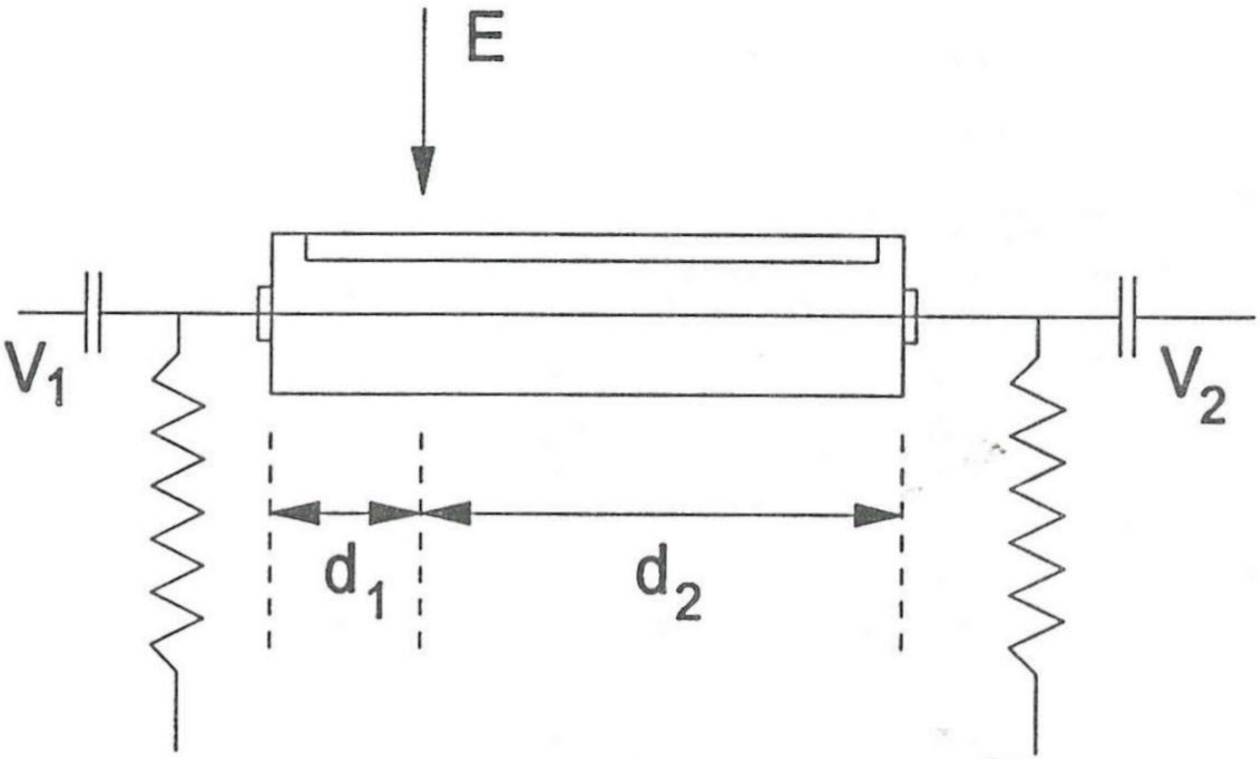


Figure 5.5. The position-sensitive detector: E = incoming X-ray photon; V_1 and V_2 = voltage at capacitors 1 and 2, respectively, d_1 and d_2 = distances from the entry point of the photon to sides 1 and 2 of the detector, respectively.

Instrumentation

B. Detectors

1b. Position-sensitive detectors (PSDs)

Advantages:

Since PSDs record data from a range of angles at once, it can be used where data acquisition speed is critical for the study of phase transformations and chemical reactions.

Disadvantages:

Resolution is lower for $2\theta \sim 0.01^{o}$.

Instrumentation

B. Detectors

2. Geiger Counter

Similar to a proportional detector except the voltage (ΔV) is increased to over 1500 V.

Not only does secondary emission occur, but also atoms are excited to emitted UV radiation.

UV photons travel at high speed and knock out other electrons in atoms causing a large avalanche.

Instrumentation

B. Detectors

2. Geiger Counter

The gas amplification factor (A) is very large (10^8 to 10^9).

Since the pulse is large, no preamp is needed, it is a stand alone detector.

Drawback - cannot handle high count rates, so used strictly as a survey meter.

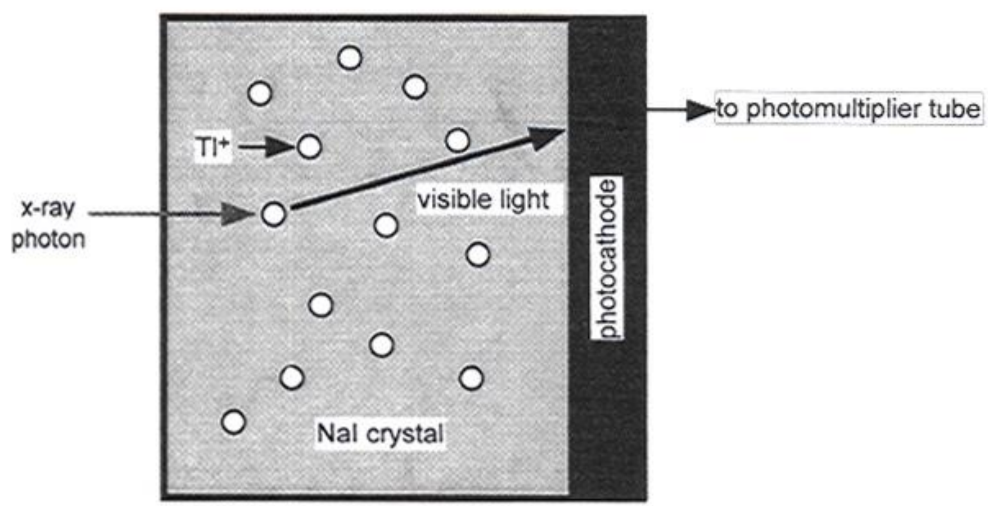
Instrumentation

B. Detectors

3. Scintillation Detector

Incident x-ray hits a crystal causing it to fluoresce.

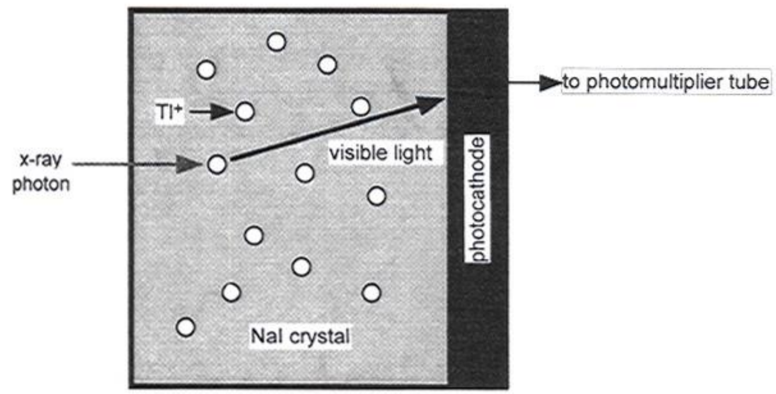
The crystal is NaI doped with 1%Tl (NaI/Tl).



Instrumentation

B. Detectors

3. Scintillation Detector



X-rays are absorbed by the crystal and raises electrons from the valence band to the conduction band in NaI.

These electrons transfer energy to the Tl^{+} ion.

Instrumentation

B. Detectors

3. Scintillation Detector

The excited Tl^{+} returns to ground state and emits light (fluoresce at λ = 420 nm).

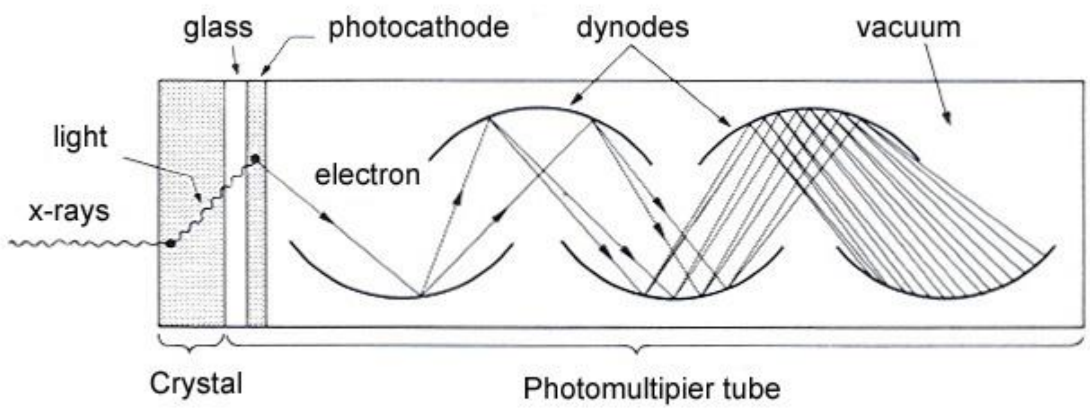
A flash of light (scintillation) purple in color is produced in the crystal and is passed into a photomultiplier tube.

Instrumentation

B. Detectors

3. Scintillation Detector

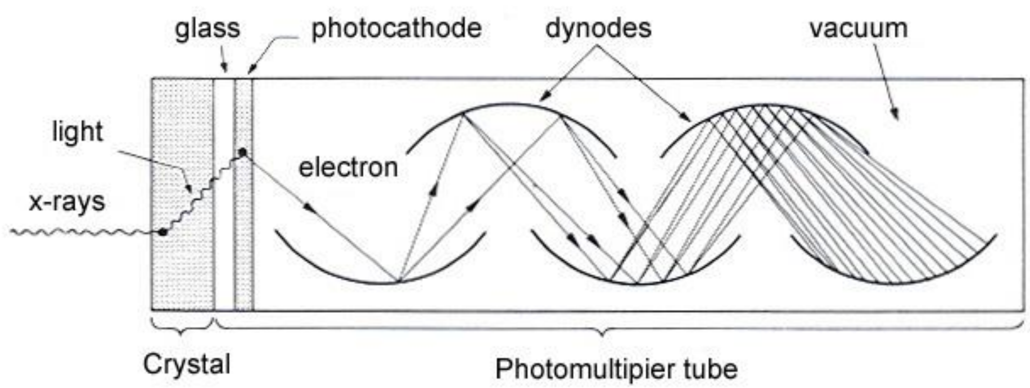
The photomultiplier tube is made up of a series (dynodes) of photocathodes.



Instrumentation

B. Detectors

3. Scintillation Detector



The photocathodes are a photosensitive material made up of cesium-antimony intermetallic compound.

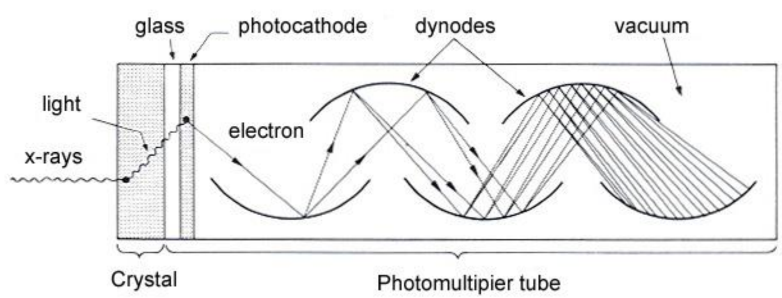
Instrumentation

B. Detectors

3. Scintillation Detector

Light strikes the 1st photocathode and electrons are ejected.

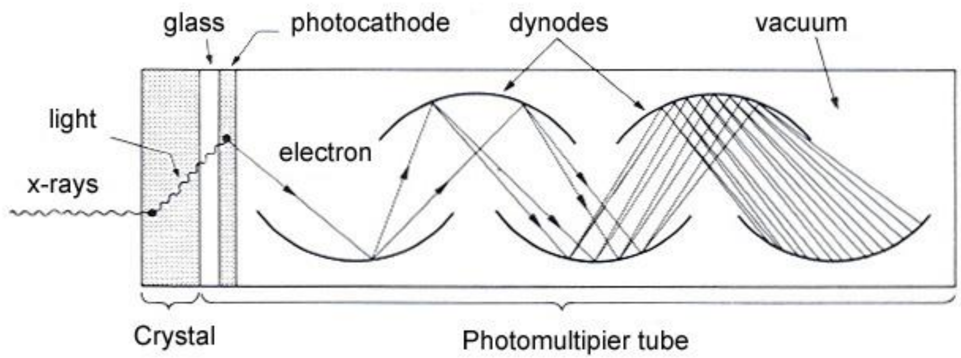
These electrons are accelerated toward the next dynode by a potential difference (ΔV)



Instrumentation

B. Detectors

3. Scintillation Detector



Each dynode is 100V more positive than the proceeding one.

As electrons hit the next dynode, more electrons are produced (multiplication).

Last dynode is connected to a circuit.

Instrumentation

B. Detectors

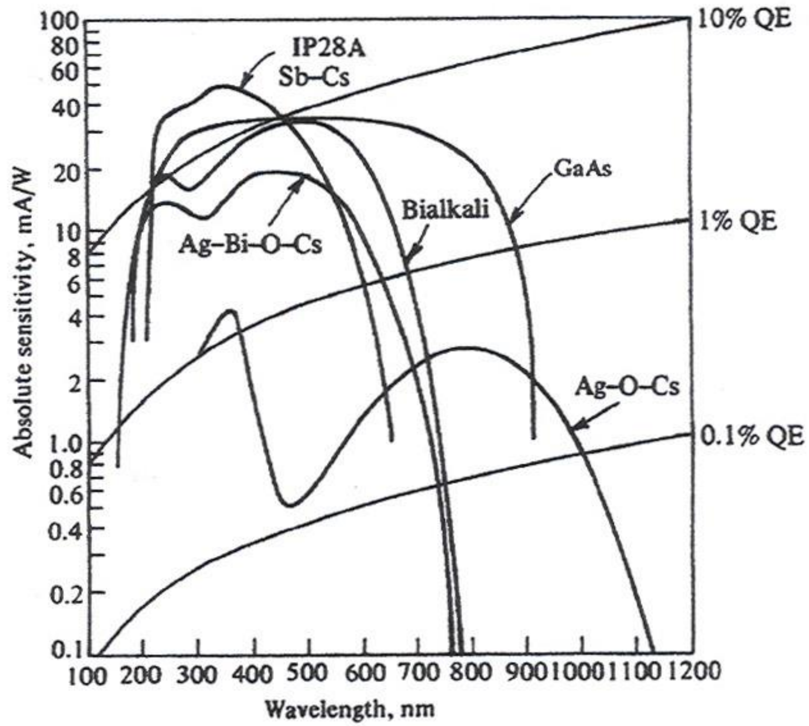
3. Scintillation Detector

Dynodes - coated with compounds such as BeO, GaP, and CsSb, which eject several electrons when subjected to the impact of a high-energy electron.

Instrumentation

Detectors

3. Scintillation Detector

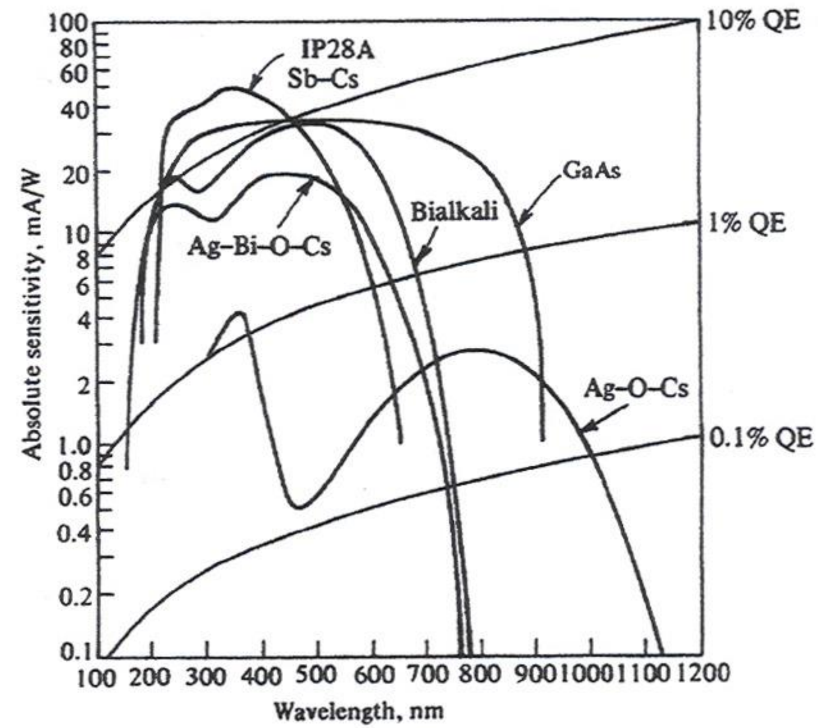


This shows the spectral sensitivity for several types of material.

Instrumentation

Detectors

3. Scintillation Detector



The Cathode Quantum Efficiency (QE) equals
QE = average # of photoelectron emitted/# of incident photons.

Instrumentation

Detectors

3. Scintillation Detector

Total Gain of the photomultiplier tube is:

$G = (f)^n$, where

f - secondary emission factor (range 3 - 50)

n - # of stages

If the Gain per dynode is ~5 (1 electron knocks out 4 to 5 electrons)

So with 10 dynodes, there is a multiplication factor of 5^{10} or 10^7.

Instrumentation

B. Detectors

3. Scintillation Detector

This whole process takes less than a μsec.

So detector can handle rates of 10^5 counts/sec without loss.

Advantage - efficient detector ~100% and low dead time ~ 0.1 μs.

Disadvantage - energy resolution is not as good as the proportional detector or a solid state detector.

Instrumentation

B. Detectors

3. Scintillation Detector

For many applications a scintillation detector will work fine.

However, some experiments will have poor data, e.g. due to the sample properties or other factors.

One cause for a bad peak-to-background ratio of a diffractogram is the bremsstrahlung background of the source radiation.

Another cause can be unwanted sample fluorescence, for example, Fe-fluorescence is frequently observed.

Instrumentation

B. Detectors

There are several methods to remove this background from the data, one is to use energy dispersive point detectors.

Example:

solid state point detectors like germanium detectors or a Si(Li) detectors.

Ge needs to be cooled to liquid nitrogen temperatures, about 77 K, and Si(Li) can be Peltier cooled.

Instrumentation

B. Detectors

But we need to discuss semiconductor technology first before learning about these types of detectors.

Instrumentation

Semiconductor technology

Silicon is a semiconductor.

A silicon atom has the electronic configuration of [Ne]3s2p2

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

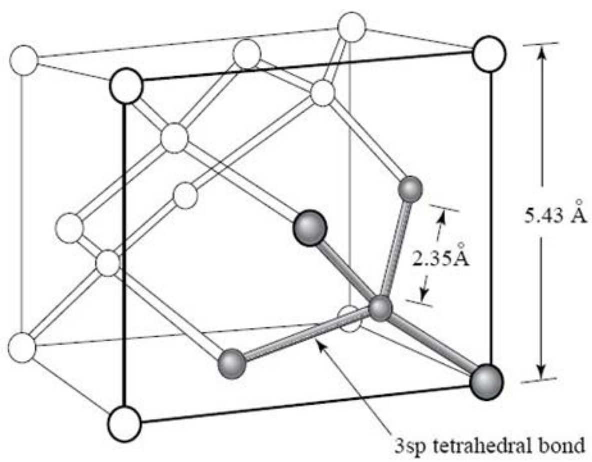
For a silicon crystal lattice the resulting structure is a tetrahedron arrangement.

Instrumentation

Semiconductor technology

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.



Instrumentation

Semiconductor technology

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, Eg (eV).

Instrumentation

Semiconductor technology

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

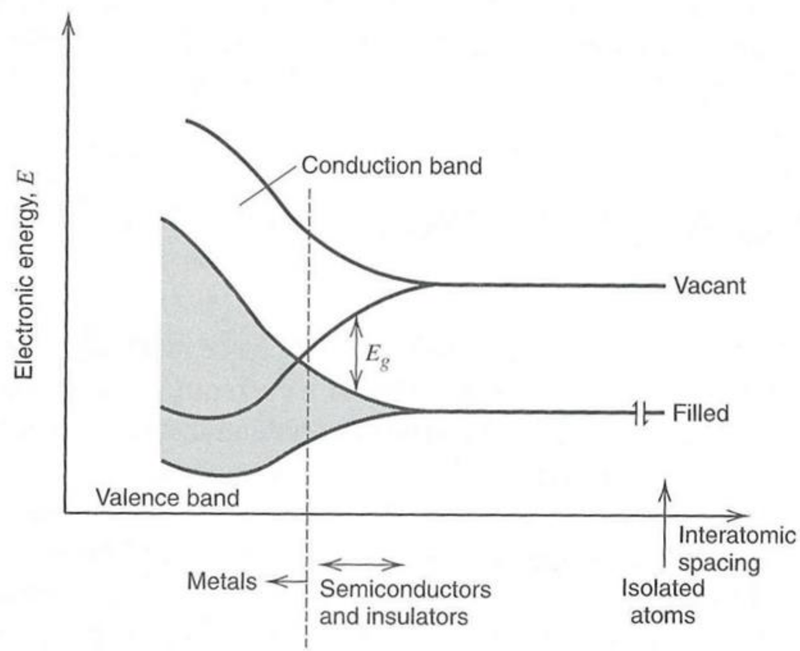


Figure 18.2.1 Formation of bands in solids (at left) by assembly of isolated atoms (characterized by orbitals at far right) into a lattice.

Instrumentation

Semiconductor technology

When the gap is very small ($E_g << kT$) 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.

If $E_g > 1.5$ eV, RT thermal excitation does not produce enough carriers for conduction.

Example:	GaP	$E_g = 2.2$ eV
	TiO_2	$E_g = 3.0$ eV

Instrumentation

Semiconductor technology

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.

Instrumentation

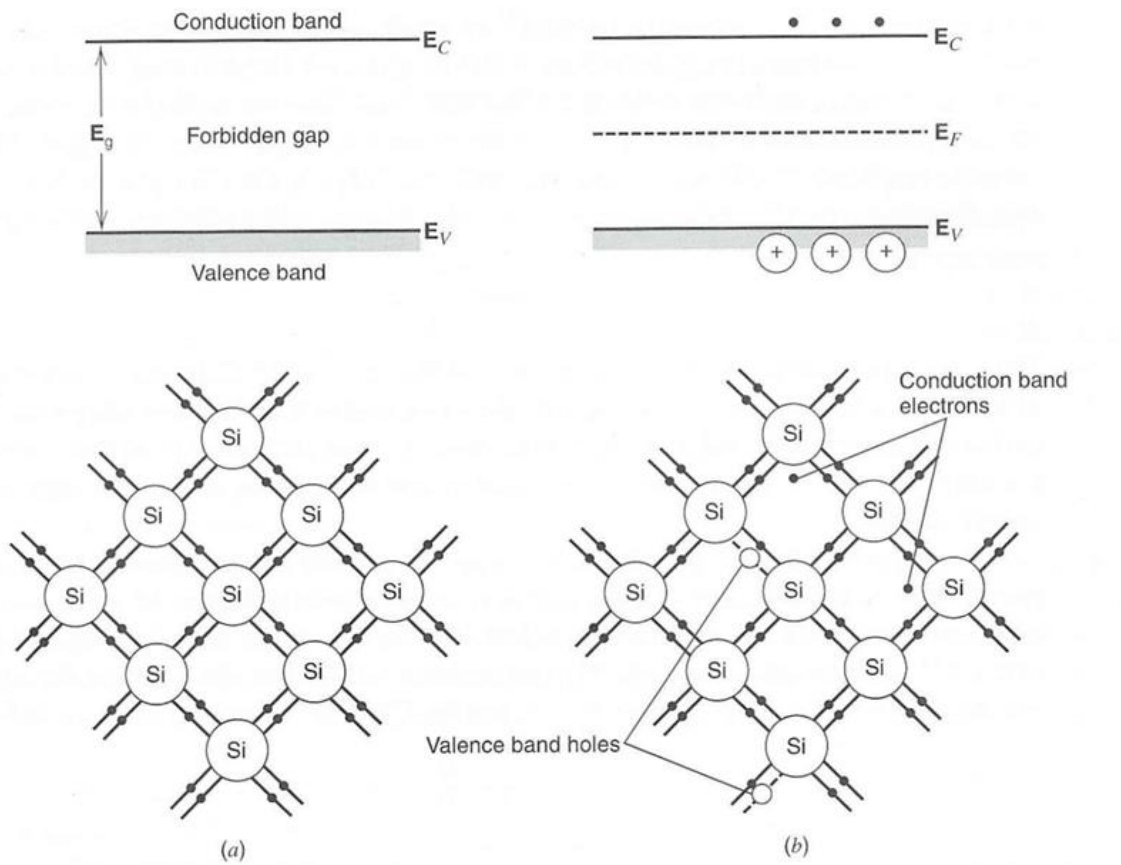


Figure 18.2.2 Energy bands and two-dimensional representation of an intrinsic semiconductor lattice. (*a*) At absolute zero (or $\mathbf{E}_g >> kT$), assuming a perfect lattice; no holes or electrons exist. (*b*) At a temperature where some lattice bonds are broken, yielding electrons in the conduction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

Instrumentation

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

ni – density for CB electrons

pi – density for VB holes

nipi = (constant)exp(-Eg/kT)

ni = pi = 2.5x1019exp(-Eg/2kT)cm-3 (near 25oC)

The mobile carriers move in the semiconductor and have mobilities of

un = 1350 cm2V-1s-1 and up = 480 cm2V-1s-1

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

Instrumentation

Semiconductor technology

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

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

Instrumentation

Semiconductor technology

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

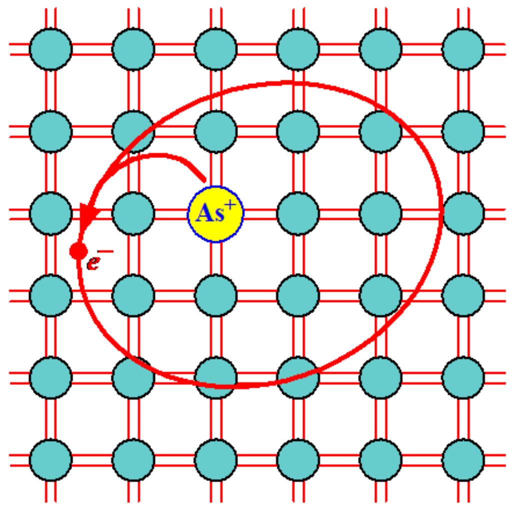


Fig. 5.9: Arsenic doped Si crystal. The four valence electrons of As allow it to bond just like Si but the fifth electron is left orbiting the As site. The energy required to release to free fifth-electron into the CB is very small.

Instrumentation

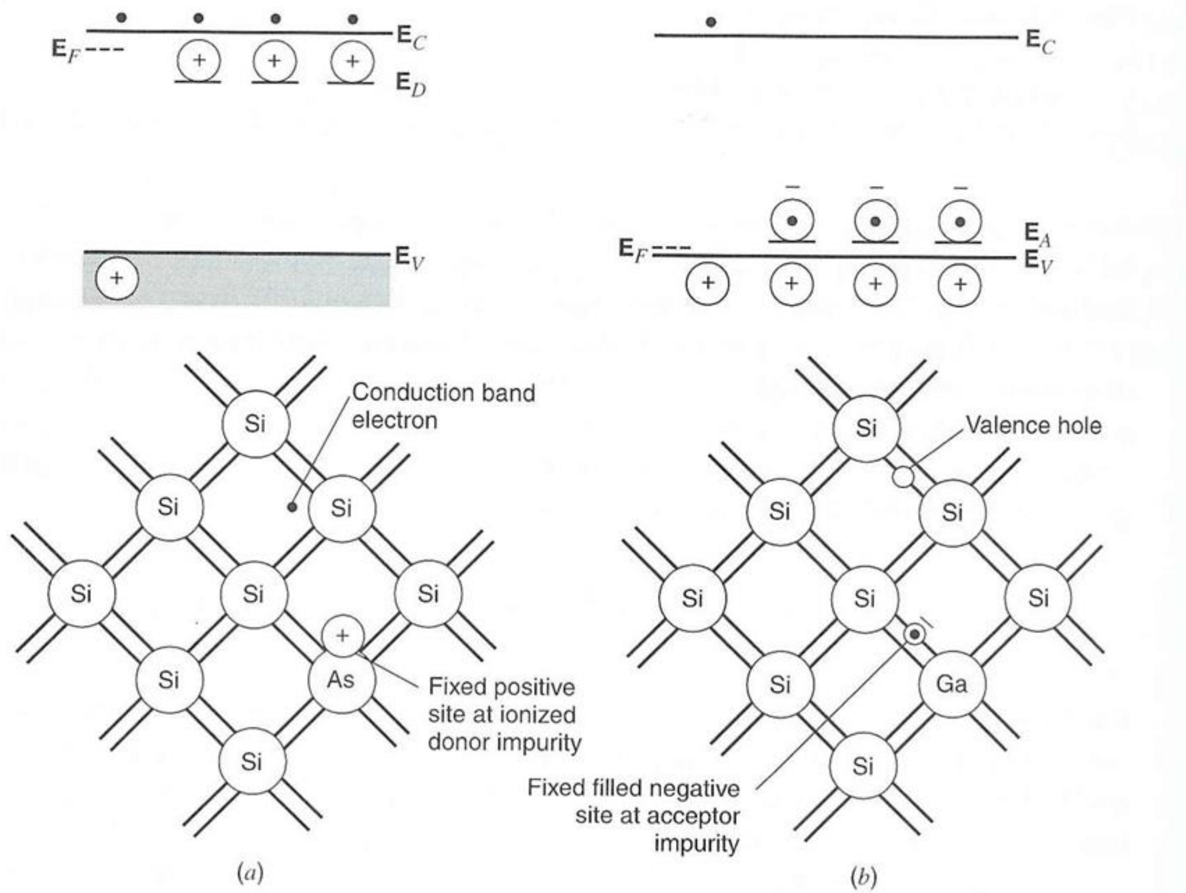


Figure 18.2.3 Energy bands and two-dimensional representation of extrinsic semiconductor lattices. (*a*) *n*-type. (*b*) *p*-type.

Instrumentation

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

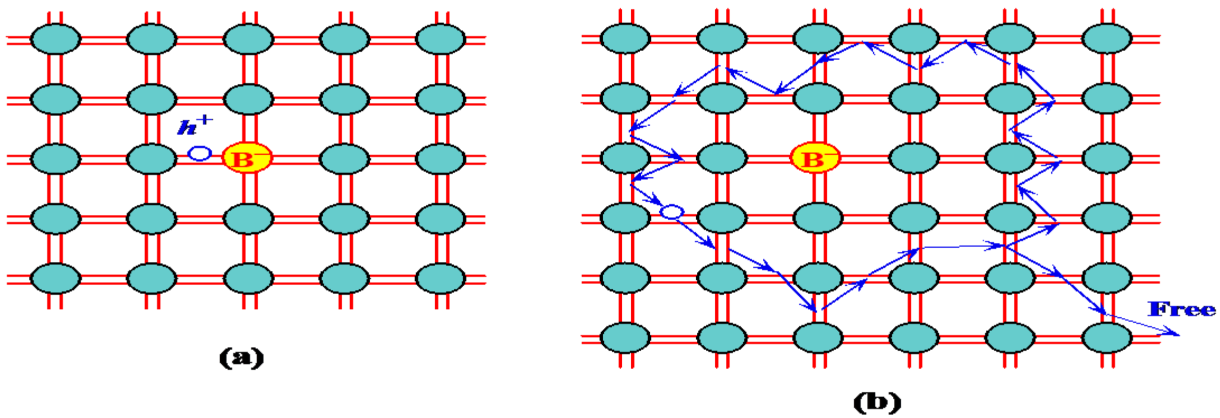


Fig. 5.11: Boron doped Si crystal. B has only three valence electrons. When it substitutes for a Si atom one of its bonds has an electron missing and therefore a hole as shown in (a). The hole orbits around the B— site by the tunneling of electrons from neighboring bonds as shown in (b). Eventually,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

Instrumentation

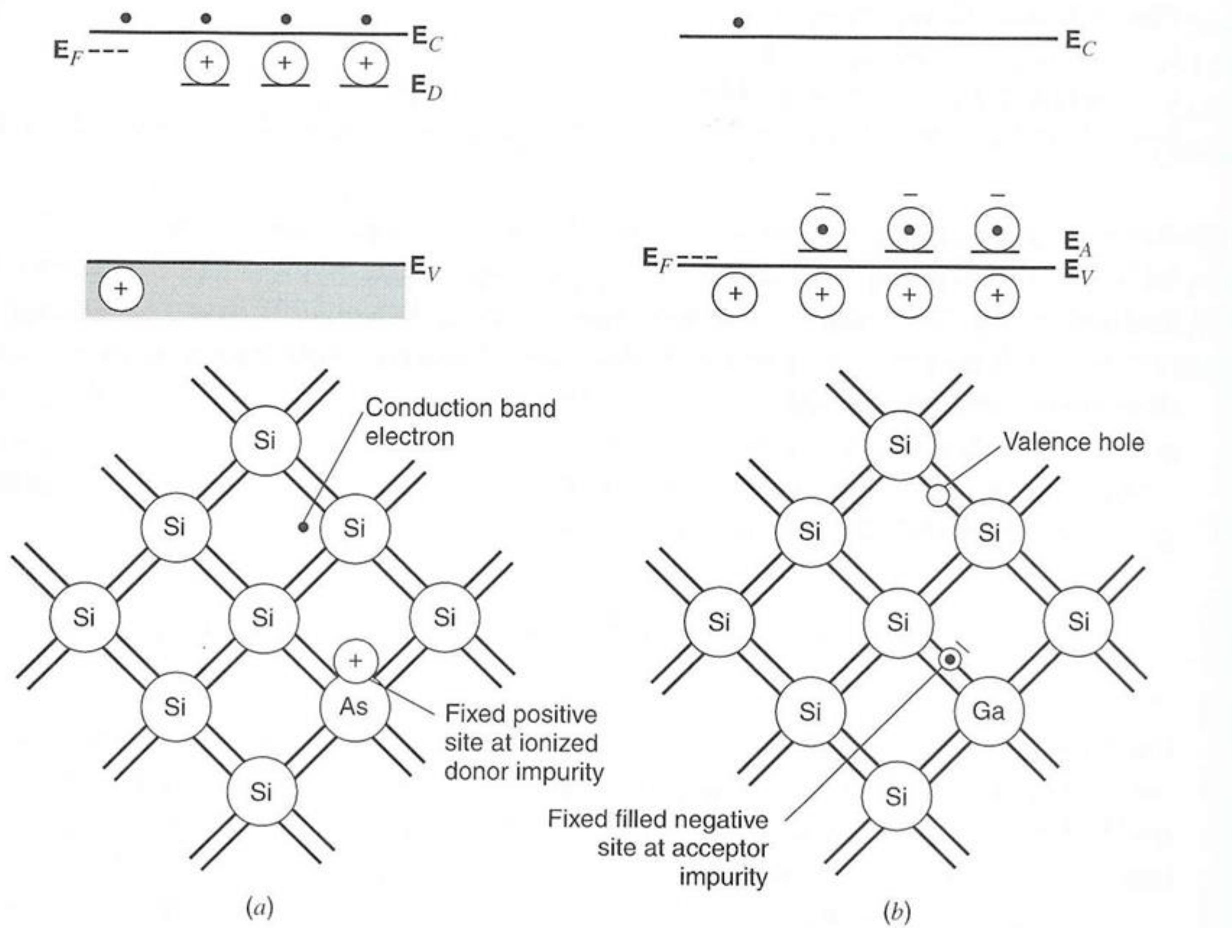


Figure 18.2.3 Energy bands and two-dimensional representation of extrinsic semiconductor lattices. (*a*) *n*-type. (*b*) *p*-type.

Instrumentation

Semiconductor technology

Thus a material doped with a donor atom is called a n-type semiconductor. Majority carriers are electrons.

Thus a material doped with a acceptor atom is called a p-type semiconductor. Majority carriers are holes.

Instrumentation

Semiconductor technology

Optical Absorption

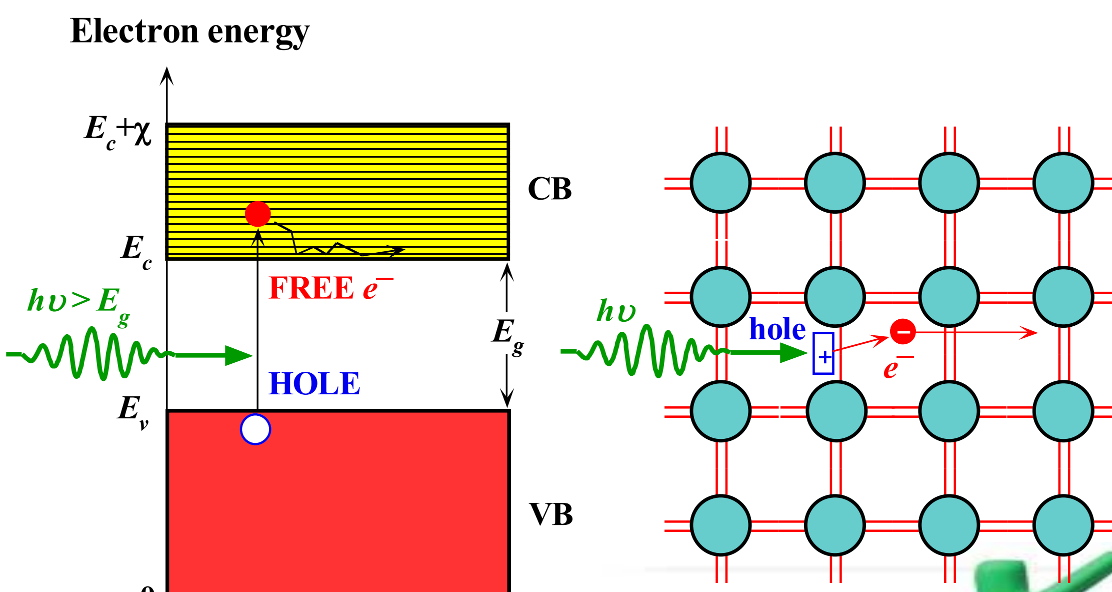
When a photon of energy higher than Eg strikes a semiconductor, electrons are excited from the VB to the CB.

Instrumentation

Semiconductor technology

A photon with energy greater than Eg can excite an electron from VB to CB.

When a Si-Si bond is broken, a free electron and a hole in the Si-Si bond is created.



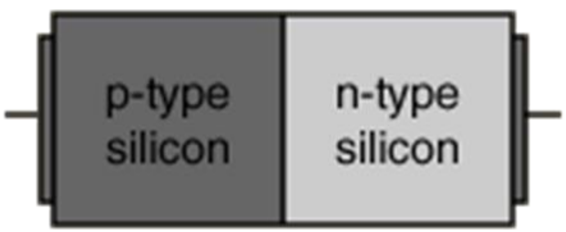
Instrumentation

Semiconductor technology

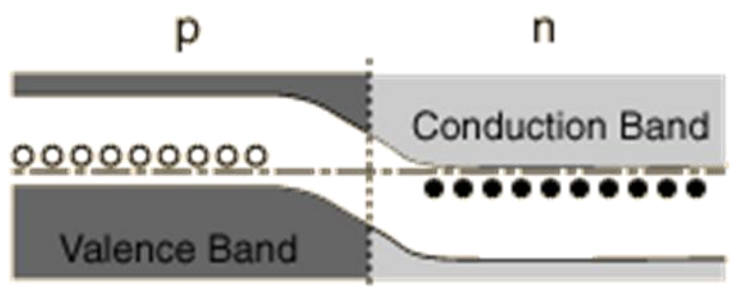
pn junctions

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

Instrumentation

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.

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

Instrumentation

Semiconductor technology

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.

Some 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.

Instrumentation

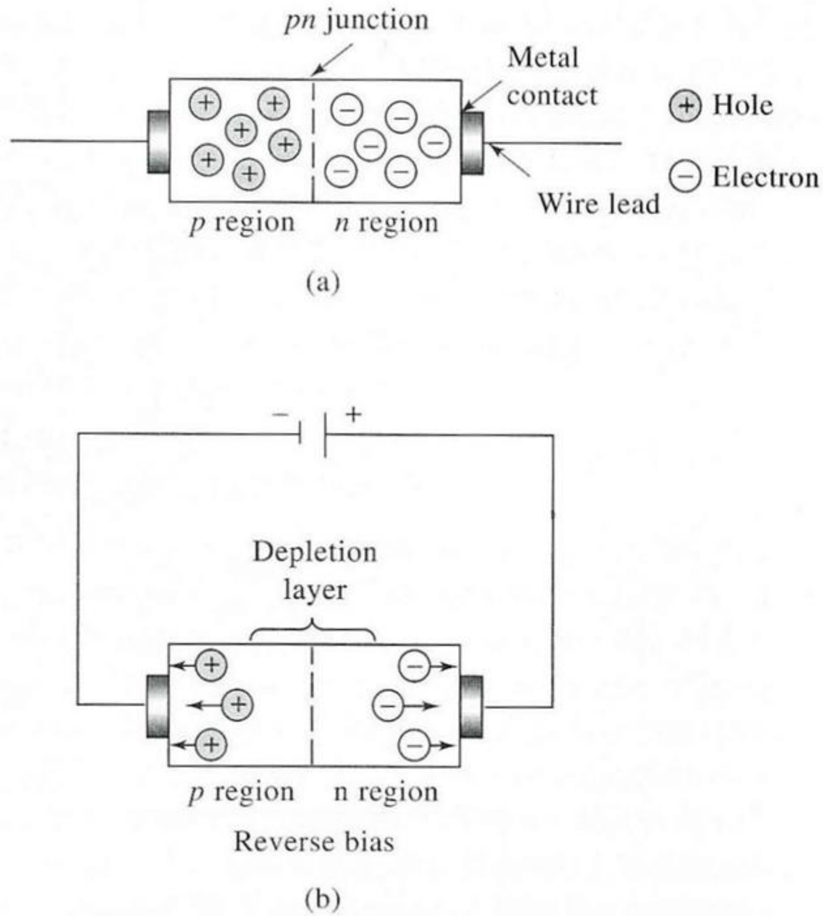


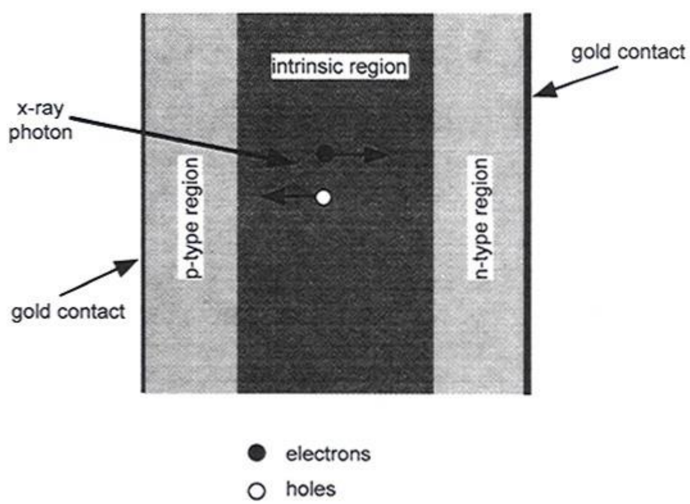
Figure 7-30 (a) Schematic of a silicon diode. (b) Formation of depletion layer, which prevents flow of electricity under reverse bias.

Instrumentation

B. Detectors

4. Solid-State Detector (Semiconductor detector)

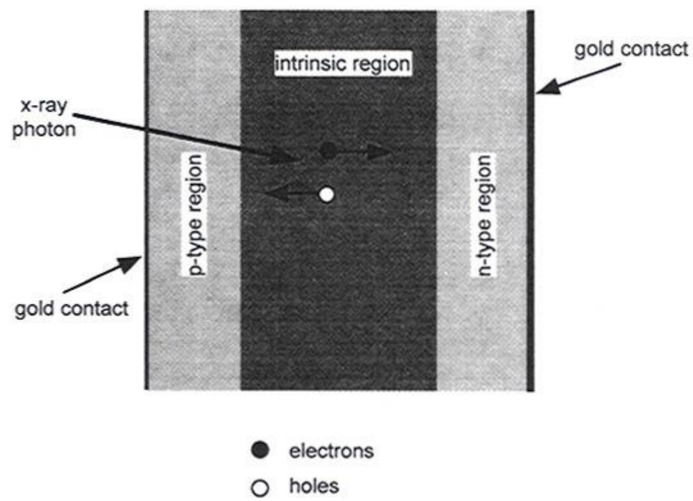
Made up of a single crystal consisting of a sandwich of intrinsic (pure) Si between a p-type layer (holes are carriers) and n-type layer (electrons are carriers). Forms a p-i-n diode.



Instrumentation

B. Detectors

4. Solid-State Detector (Semiconductor detector)



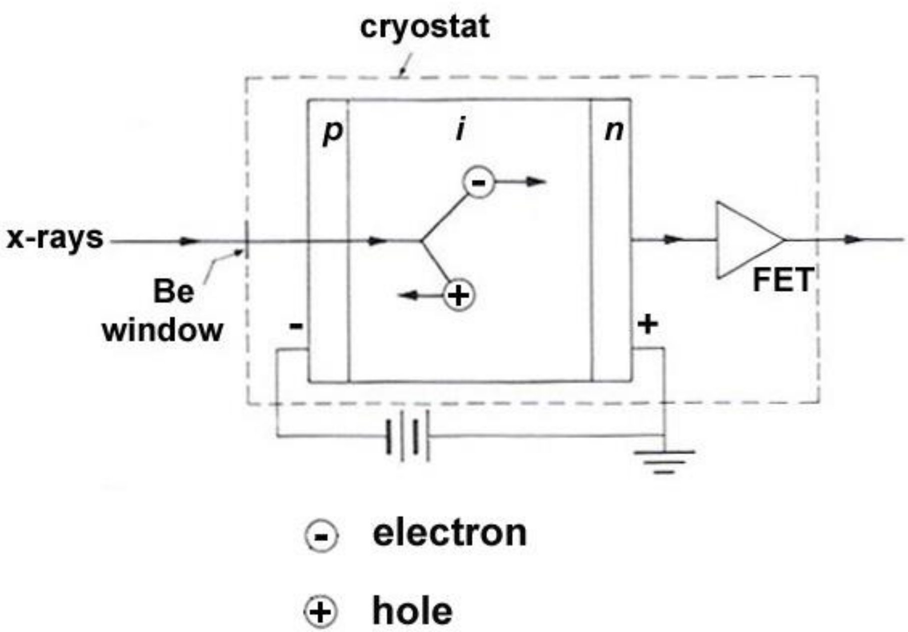
The solid-state detector is made by taking Si (3-5 mm thick and 5-15 mm in diameter) that is lightly doped with boron (p-type).

Instrumentation

B. Detectors

4. Solid-State Detector (Semiconductor detector)

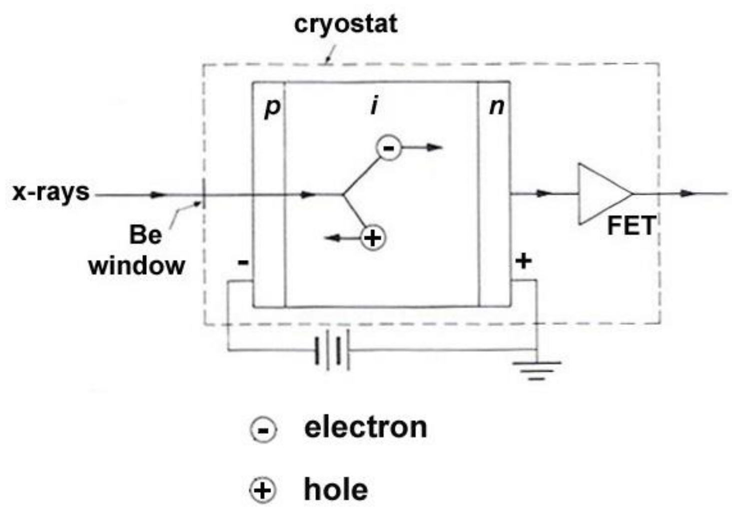
Li is applied to one face of the silicon and allowed to diffuse into the crystal at an elevated temperature.



Instrumentation

Detectors

4. Solid-State Detector (Semiconductor detector)



A gradient occurs, with one side higher in Li+ concentration than the other.

A bias is applied to create the p-i-n diode.

Instrumentation

Detectors

4. Solid-State Detector (Semiconductor detector)

When an x-ray photon hits the detector, electron-hole pairs are produced in the Si.

These pairs are created when an energy of 3.8 eV (indirect gap of silicon) is exceeded.

Number of electron-hole pairs, n equals:

n = energy of the photon/energy required to create one pair

For a CuKα photon, n = 8040/3.8 = 2116 pairs

Instrumentation

Detectors

4. Solid-State Detector (Semiconductor detector)

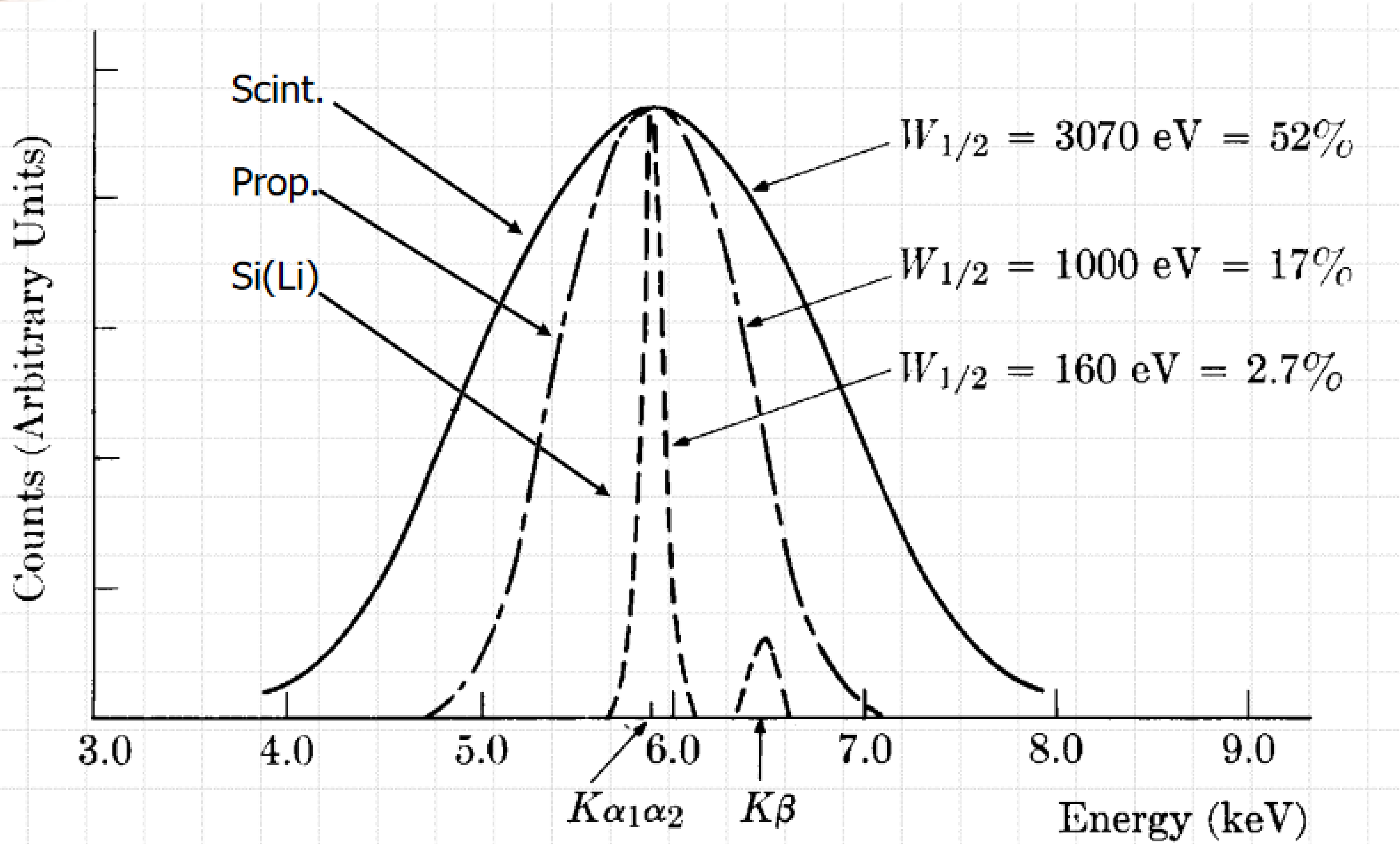
The electron-hole pairs are swept to opposite poles by a bias, and the current is directed into a counting circuit.

Si(Li) detectors achieve a typical energy resolution of about 300 eV at 5.9 keV, which is sufficient to discriminate the iron line at 6.4 keV from the copper line at 8 keV.

Small signal requires a charge-sensitive preamp integrated with the detector.

Due to thermal e/h generation and noise in the preamp, cooling the detector is needed.

Instrumentation



Instrumentation

Detectors

4. Solid-State Detector (Semiconductor detector)

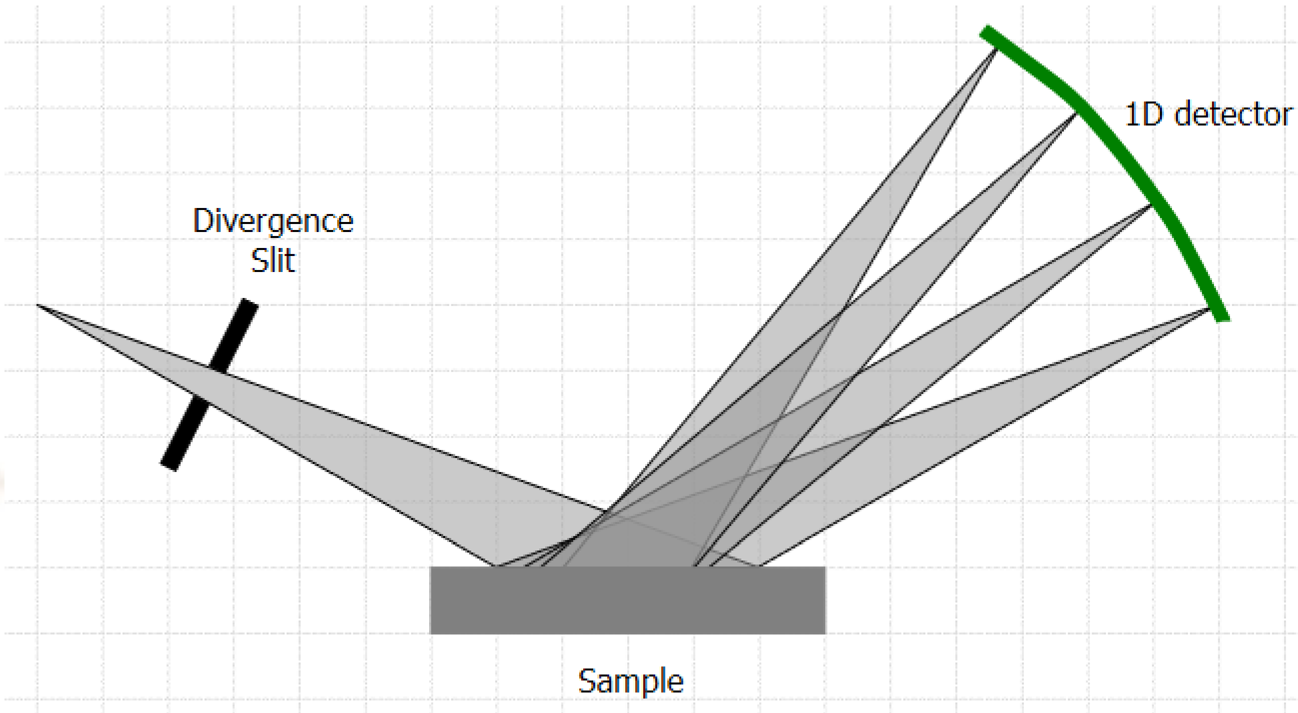
Advantage- excellent energy resolution, can resolve some fluorescence problems and Kα and Kβ

Disadvantage – must use bulky dewar to keep detector cool (to reduce noise), long dead time, easy to overwhelm the detector.

Some newer detectors are using Si p-i-n photodiodes and large bandgap materials (CdTe and CdZnTe) for room-temperature operation.

Instrumentation

B. Detectors



Instrumentation

Detectors

4. Solid-State Detector (Semiconductor detector)

The <u>Peltier effect</u> 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.

Instrumentation

Detectors

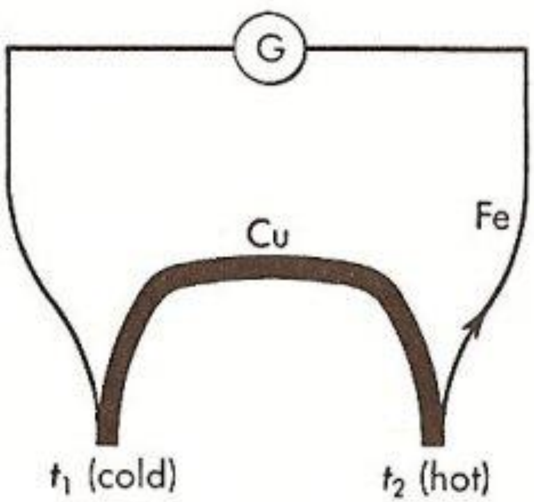
4. Solid-State Detector (Semiconductor detector)

Seebeck effect

Seebeck observed that an electrical current is present in a series circuit of two dissimilar metals, provided the junctions of the two metals are at different temperatures.

The thermoelectric effect increases as t2 - t1 increases.

He investigated the thermoelectric properties of a large number of metals and arranged them in a thermoelectric series.



Instrumentation

Detectors

4. Solid-State Detector (Semiconductor detector)

The <u>Peltier effect</u> is the reverse of the Seebeck effect; a creation of a heat difference from an electric voltage.

This effect was observed in 1834 by Jean Peltier, 13 years after Seebeck's initial discovery.

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

Instrumentation

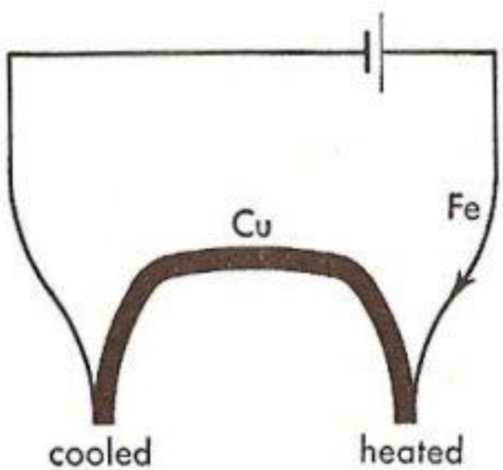
Detectors

4. Solid-State Detector (Semiconductor detector)

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.



Instrumentation

Detectors

4. Solid-State Detector (Semiconductor detector)

The <u>Peltier effect</u> can also occurs 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.

Instrumentation

Detectors

4. Solid-State Detector (Semiconductor detector)

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).

Instrumentation

B. Detectors

5. Two Dimensional Detectors

Real time image intensifier

X-rays scattered from a sample strike a phosphor (ZnS:Ni, GdOS2; Tb, etc.) screen and emit visible light.

The visible signal can be amplified and captured using a charge-coupled device (CCD) video camera.

Instrumentation

B. Detectors

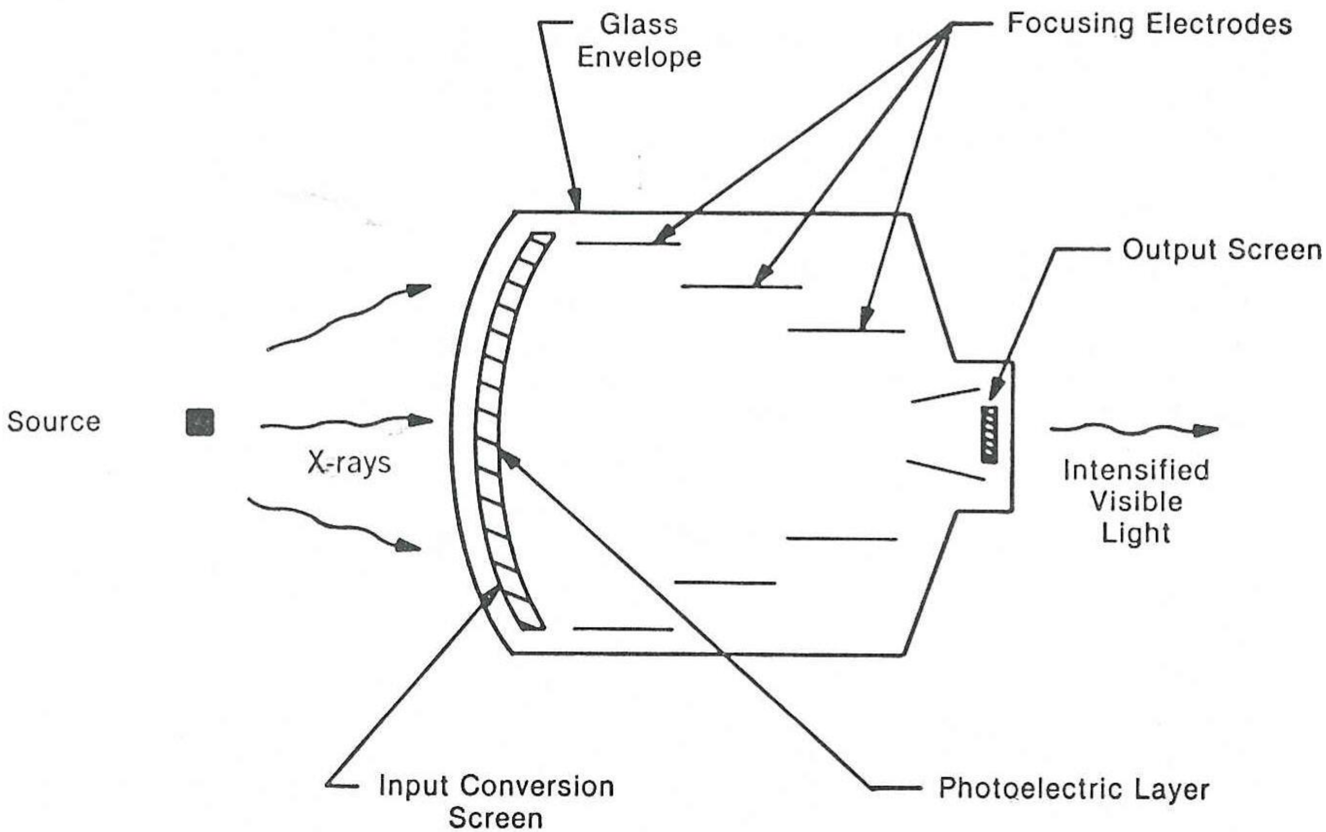
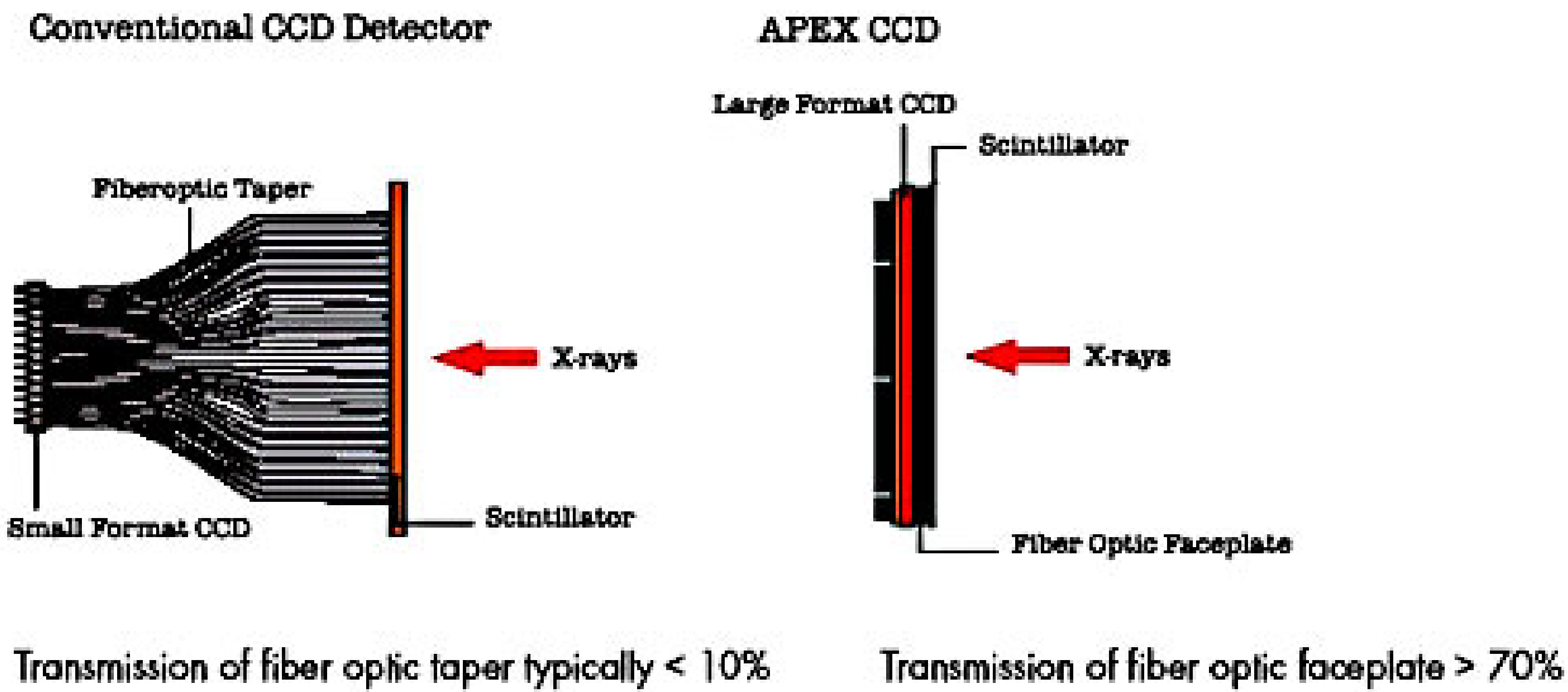


Figure 5.13. An image intensifier. From Jenkins [1, p. 22]. Copyright © 1988, John Wiley & Sons, Inc. Reprinted by permission of the publisher.

Instrumentation



In the conventional CCD design, more than 90% of the photons from the scintillator are lost in the fiber optic taper.
In the APEX II detector, 1:1 imaging improves the optical transmission by an order of magnitude - allowing data on yet smaller microcrystals or very weak diffractors. The APEX II has 15 times the sensitivity of the classic design.

Instrumentation

B. Detectors

5. Two Dimensional Detectors

Advantages:

-moderate cost

-real-time display of images

-allow computer enhancement of image

Disadvantages:

- poorer resolution than film

Instrumentation

B. Detectors

5. Two Dimensional Detectors

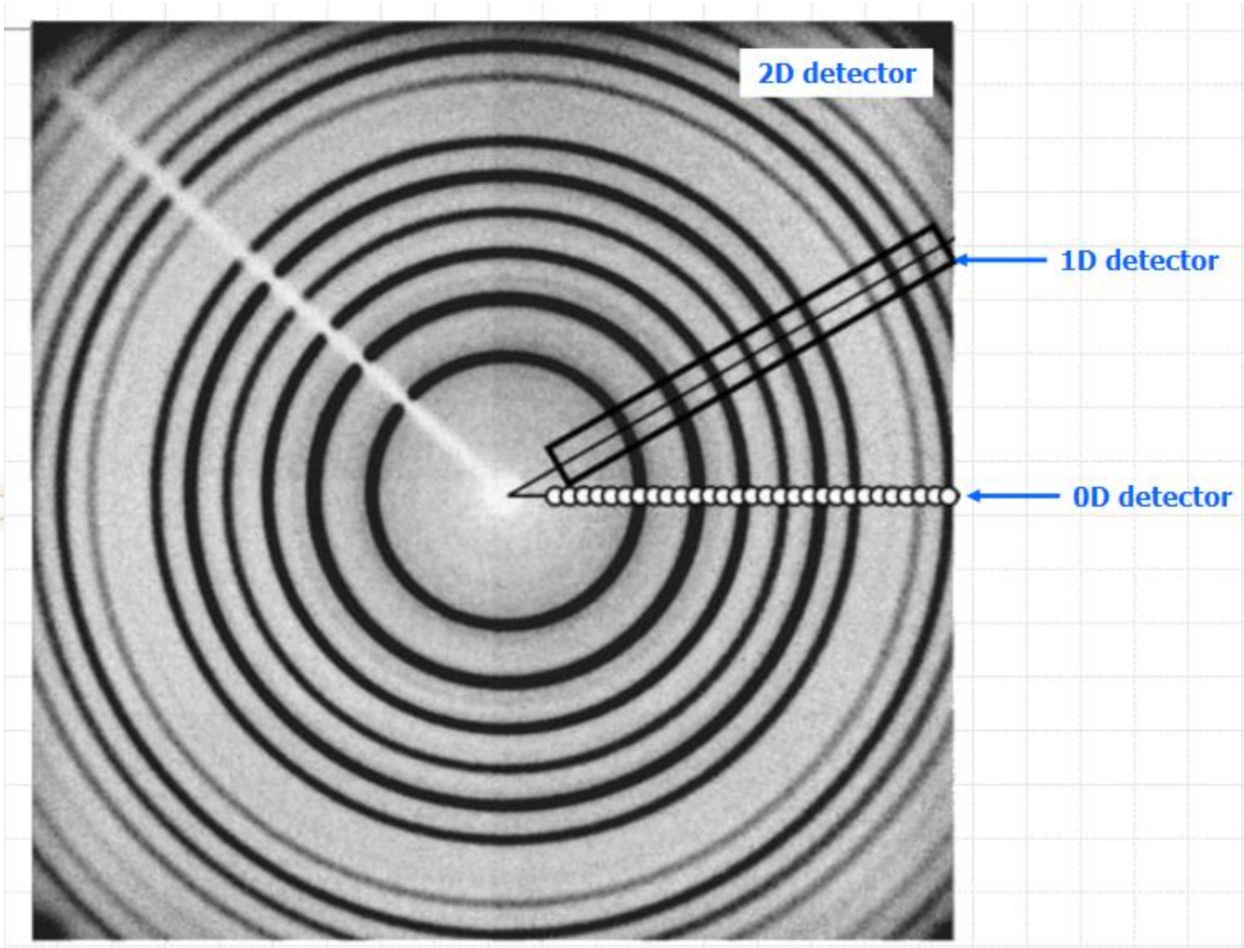
Two dimensional position sensitive detector

similar to PSDs but use a 2-D array to offer high speed and good resolution.

Cost has decreased from $150,000 a few years ago to ~$60,000 now.

Instrumentation

B. Detectors



Instrumentation

B. Detectors

Properties:	Point detector	Line detector	Area detector
Irradiated area	From large to small	From large to small	Small
Sample information	Integral	Integral	Small spot (micro-diffraction)
Influence of preferred orientation and grain size effects	Not directly visible	Not directly visible	Directly visible (spotty rings)
Angular resolution	Excellent	Excellent	Moderate to excellent
Data recording speed	Low	High	High
Energy resolution	Very high	High	Low to high
Linearity	High	High to very high	Moderate to very high

Instrumentation

B. Detectors

Application	Point detector	Line detector	Area detector
Phase identification	Yes	Yes	Yes
Quantification based on one or a few peaks	Yes	Yes	Yes
Quantification based on full pattern analysis	Yes, but slow	Yes	Yes
Residual stress	Yes (especially with parallel beam geometry)	Yes	Yes
Texture	Yes	Yes	Yes
Micro-diffraction	Yes, but slow	Yes	Yes
Reflectivity	Yes	Yes	No

Instrumentation

B. Detectors

6. Counting Electronics

Pulse height selector

Size of voltage pulse is proportional to energy of x-ray photon, so when different λ's are incident on proportional detector, different voltage sizes are generated.

Can electronically discriminate these pulses by pulse height selection (PHS) using a pulse height analyzer (PHA).

Instrumentation

Detectors

6. Counting Electronics

<u>Pulse height selector</u>

PHA – contains two discriminators and an anticoincidence unit, with this, pulse voltages higher and lower than the desired signal can be eliminated.

Advantage – removal of sample fluorescence and background.

Instrumentation

Detectors

6. Counting Electronics

<u>Scaler/Timer and Ratemeter</u>

After a pulse is processed by the PHA, it is passed on to 2 independent circuits:

-scaler/timer

-ratemeter

Instrumentation

Detectors

6. Counting Electronics

Scaler/Timer and Ratemeter

Scaler/timer – counts the number of pulses (N) arriving at any time interval (t).

N and t may be measured independently.

Ratemeter – takes in random arrival of pulses and puts out an average signal to display on a calibrated voltmeter.

Instrumentation

Detectors

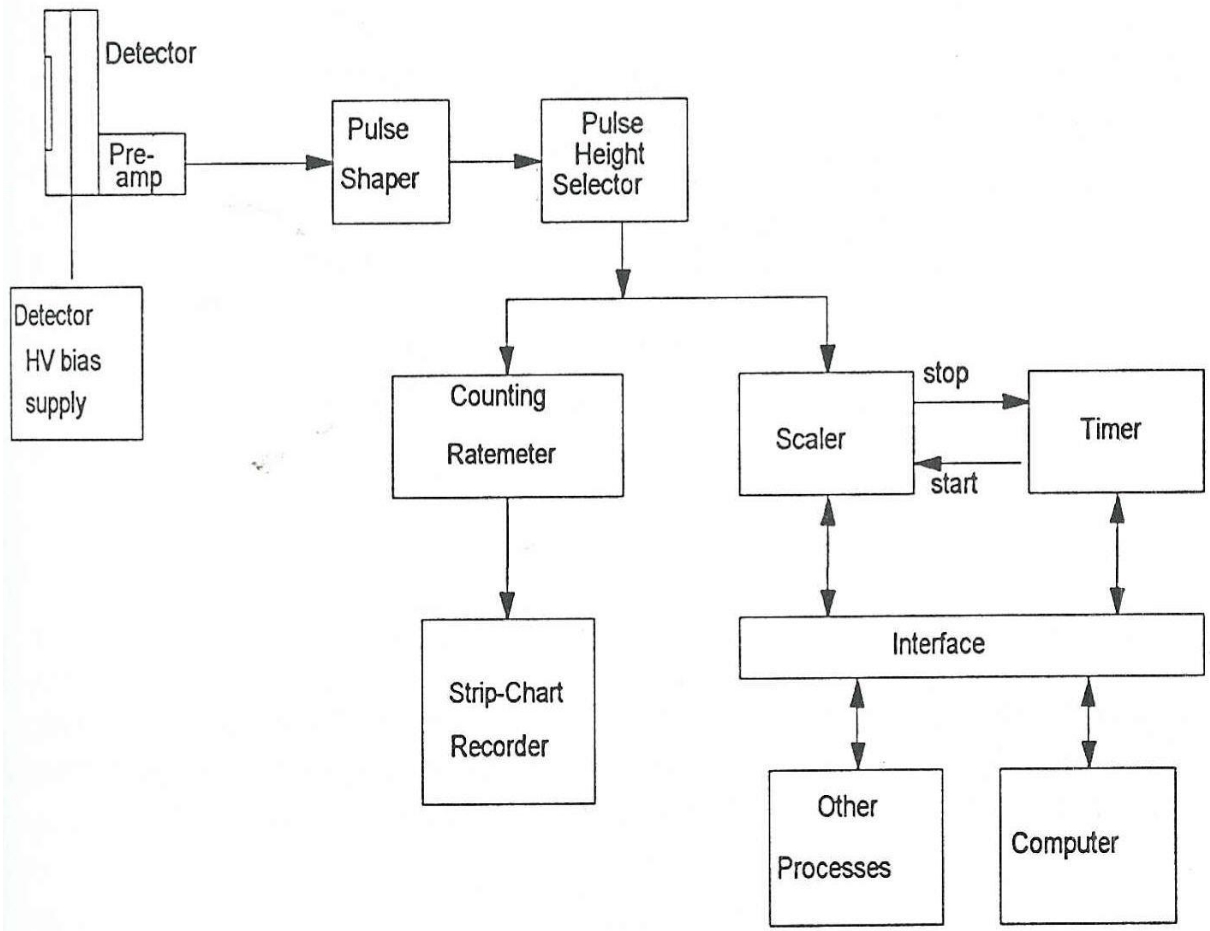


Figure 5.10 Signal-processing electronics.

Instrumentation

Reading Assignment:

Read Chapter 4, 5, 9 and 13 from:

-Introduction to X-ray powder Diffractometry by Jenkins and Synder

Read Chapter 6, 13, and 14 from

-Elements of X-ray Diffraction by Cullity and Stock

chem 5390

Advanced X-ray Analysis