

**DEPARTMENT OF PHYSICS AND NANOTECHNOLOGY
SRM INSTITUTE OF SCIENCE AND TECHNOLOGY**

18PYB103J –Semiconductor Physics

Module-IV Lecture-14

**FUNDAMENTAL LAWS OF ABSORPTION &
INSTRUMENTATION OF UV-VIS SPECTROSCOPY**



- The light source is passed through the setup, measurements are recorded for incident and transmitted radiations.
- These measurements are used to calculate the transmission and absorption spectra of the material.
- While many modern instruments perform Beer's law calculations by simply comparing a test sample with a reference sample which have a negligible absorbance.
- The graphing method assumes a straight-line relationship between absorbance and concentration, which is valid only for dilute solutions.

Transmittance, $T = I/I_0$

Absorbance, $A = 2 - \log(\%T)$

I – Transmitted radiation intensity

I_0 – Incident radiation intensity



- When the light beams are passed through a dilute sample, the absorption will be less since there is only less number of absorbing particles presented.
- The light beam was passed through a concentrated sample.
- The intensity of the transmitted beam was considerably low, which leads to violation of Beer Lambert's law.
- The law thus states that for a dilute solution, $A = Kcl$

Where,

A – absorbance

K – molar absorbance coefficient

c– molar concentration

l - Path length



- Basic principle of spectroscopy is the Beer-Lambert's law (also known as beer's law) that relates the attenuation of light to the properties of the material through which the light is travelling.
- Lambert's law stated that absorbance of a material is directly proportional to its thickness (path length).
- Much later, August Beer discovered another attenuation relation in 1852. Beer's law stated that absorbance is proportional to the concentrations of the material sample.
- The modern derivation of the Beer–Lambert law combines the two laws and correlates the absorbance to both the concentrations and the thickness of the material.
- Absorption spectra of chemical samples are generated when a beam of electromagnetic radiation is passed through a sample, and the chemical sample absorbs a portion of the photons of electromagnetic energy passing through the sample.



Spectrophotometry is a method to measure how much a chemical substance absorbs light by measuring the intensity of light as a beam of light passes through sample solution. The basic **principle** is that each compound absorbs or transmits light over a certain range of wavelength.

The **Beer-Lambert law** is the linear relationship between **absorbance** and concentration of an **absorbing** species. The **Beer-Lambert law** implies that both the type and the concentration of the molecules are important in the process of radiation **absorption**.



- Spectroscopy is the measurement and interpretation of electromagnetic radiation absorbed or emitted when the molecules or atoms or ions of a sample moves from one energy state to another energy state.
- UV spectroscopy is type of absorption spectroscopy in which light of ultra-violet region (200-400 nm) is absorbed by the molecule which results in the excitation of the electrons from the ground state to higher energy state.
- Most of the organic molecules and functional groups are transparent in the portion of the electromagnetic spectrum that we call the uv and visible regions
- In that region where wavelengths range from 190nm to 800nm
- This information, when combined with the detail provided by infrared and nuclear magnetic resonance (NMR) spectra, can lead to valuable structural proposals.

Principle of UV Spectroscopy

- Basically, spectroscopy is related to the interaction of light with matter.
- As light is absorbed by matter, the result is an increase in the energy content of the atoms or molecules.
- When ultraviolet radiations are absorbed, this results in the excitation of the electrons from the ground state towards a higher energy state.
- Molecules containing π -electrons or non-bonding electrons (n-electrons) can absorb energy in the form of ultraviolet light to excite these electrons to higher anti-bonding molecular orbitals.
- The absorption of ultraviolet light by a chemical compound will produce a distinct spectrum which aids in the identification of the compound.

Instrumentation of UV Spectroscopy

Light Source

- Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region.
- Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm.

Sample and reference cells

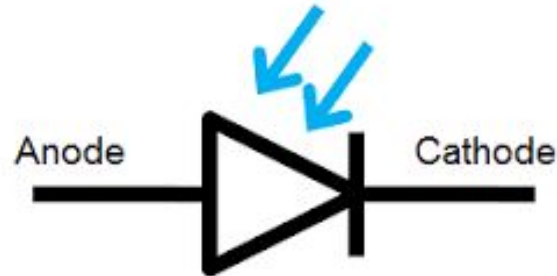
- One of the two divided beams is passed through the sample solution and second beam is passé through the reference solution.
 - Both sample and reference solution are contained in the cells.
 - These cells are made of either silica or quartz. Glass can't be used for the cells as it also absorbs light in the UV region.
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- Generally two photocells serve the purpose of detector in UV spectroscopy.
 - One of the photocell receives the beam from sample cell and second detector receives the beam from the reference.
 - The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

Monochromator

- Monochromators generally is composed of prisms and slits.
- Most of the spectrophotometers are double beam spectrophotometers.
- The radiation emitted from the primary source is dispersed with the help of rotating prisms.
- The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose.
- The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.

Detector

Photo-diode symbol



- A photo detector is a semiconductor device which converts light energy to electrical energy.
- It consists of a simple P-N junction diode and is designed to work in reverse biased condition.
- The photons approaching the diode are absorbed by the photodiode and current is generated.
- It can be made by diffusing a p-type impurity into a n-type bulk silicon wafer or vice versa.

- The defused area is called active photodiode area which is coated by an anti reflecting thin film for maximum detection and is covered by an illumination window.
- Non active area is deposited by thick layer of silicon oxide. Some photodiodes are manufactured with built-in filters and lenses having different surface areas.
- Response time of the photodiode is inversely proportional to the surface area. Solar cell is one of the best examples for photodiode.
- To increase the speed of response, a PIN junction is used instead of P-N junction

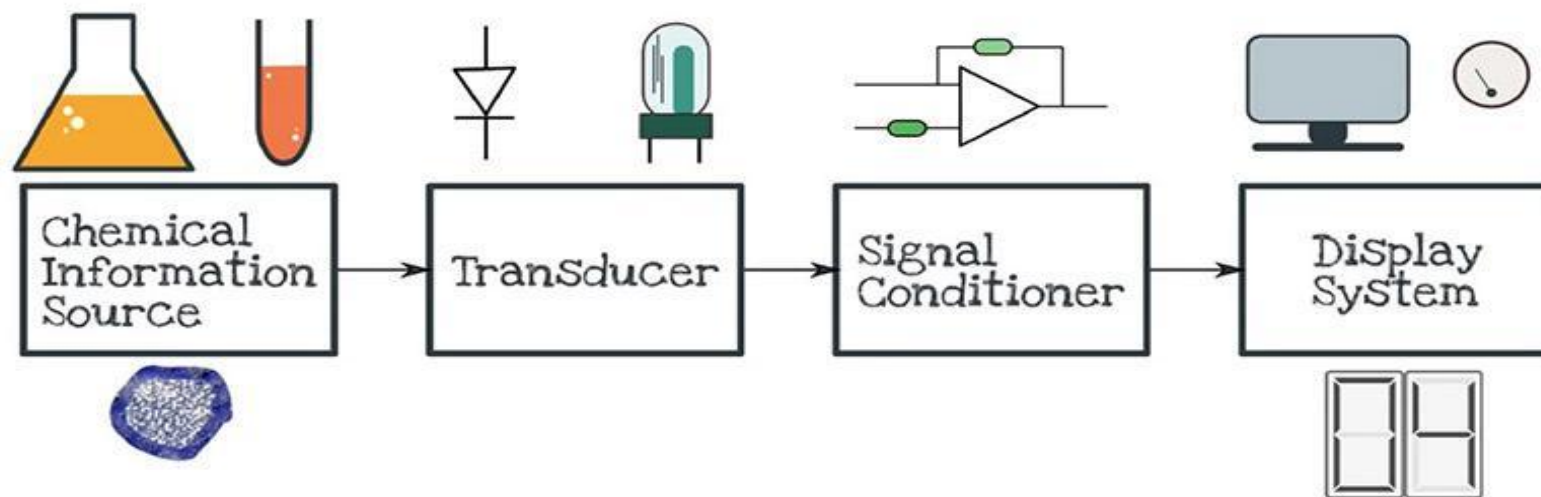


Amplifier

- The alternating current generated in the photocells is transferred to the amplifier.
- The amplifier is coupled to a small servometer.
- Generally current generated in the photocells is of very low intensity, the main purpose of amplifier is to amplify the signals many times so we can get clear and recordable signals.

Recording devices

- Most of the time amplifier is coupled to a pen recorder which is connected to the computer.
- Computer stores all the data generated and produces the spectrum of the desired compound.



UV-VISIBLE SPECTROSCOPY

Applications of UV Spectroscopy

Detection of Impurities

- Best methods for determination of impurities in organic molecules.
- Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material.
- By also measuring the absorbance at specific wavelength, the impurities can be detected.

Structure elucidation of organic compounds

- It is useful in the structure elucidation of organic molecules, such as in detecting the presence or absence of unsaturation, the presence of hetero atoms.
- UV absorption spectroscopy can be used for the **quantitative determination of compounds** that absorb UV radiation.

Applications of UV Spectroscopy

- UV absorption spectroscopy can characterize those types of compounds which absorb UV radiation thus used in qualitative determination of compounds. Identification is done by comparing the absorption spectrum with the spectra of known compounds.
- This technique is used to detect the presence or absence of functional group in the compound. Absence of a band at particular wavelength regarded as an evidence for absence of particular group.
- Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed.

- Many drugs are either in the form of raw material or in the form of formulation. They can be assayed by making a suitable solution of the drug in a solvent and measuring the absorbance at specific wavelength.
- Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds.
- UV spectrophotometer may be used as a detector for HPLC.