

## Ultraviolet-Visible Spectroscopy to determine the nature of band gap and estimation of the bandgap

**Objectives: Estimation of the band gap for direct and indirect band gap materials using Uv-Vis spectra**

### Theory: Direct and Indirect Band Gap Semiconductors

The band gap represents the minimum energy difference between the top of the valence band and the bottom of the conduction band. However, the top of the valence band and the bottom of the conduction band are not generally at the same value of the electron momentum ( $k$ ). In a **direct band gap semiconductor**, the top of the valence band and the bottom of the conduction band occur at the same value of momentum ( $k$ ), as in the schematic below.

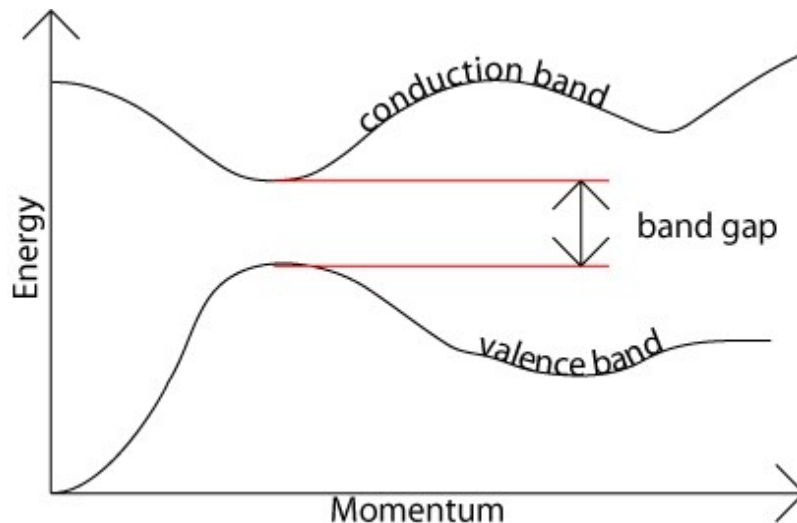


Fig.1. Schematic of band structure for direct band gap material

In an **indirect band gap semiconductor**, the maximum energy of the valence band occurs at a different value of momentum to the minimum in the conduction band energy:

The difference between the two is most important in optical devices. Each photon of energy  $E$  has momentum  $p = E / c$ , where  $c$  is the velocity of light. An optical photon has an energy of the order of  $10^{-19}$  J, and, since  $c = 3 \times 10^8$   $\text{ms}^{-1}$ , a typical photon has a very small amount of momentum.

A photon of energy  $E_g$ , where  $E_g$  is the band gap energy, can produce an electron-hole pair in a direct band gap semiconductor quite easily, because the electron does not need to be given very much momentum. However, an electron must also undergo a significant

change in its momentum for a photon of energy  $E_g$  to produce an electron-hole pair in an indirect band gap semiconductor. This is possible, but it requires such an electron to interact not only with the photon to gain energy, but also with a lattice vibration called a phonon in order to either gain or lose momentum.

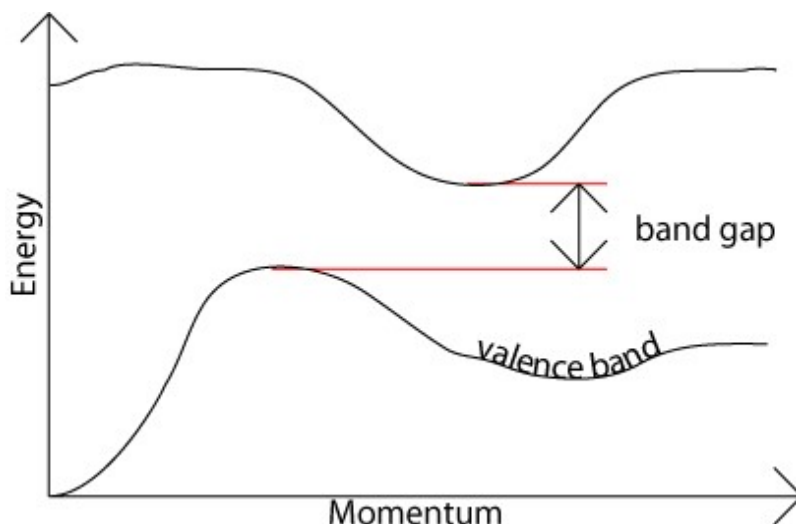


Fig.2. Schematic of band structure for indirect band gap material

The indirect process proceeds at a much slower rate, as it requires three entities to intersect in order to proceed: an electron, a photon and a phonon. The same principle applies to recombination of electrons and holes to produce photons. The recombination process is much more efficient for a direct band gap semiconductor than for an indirect band gap semiconductor, where the process must be mediated by a phonon. Even though broad spectrum of phonons is available in a crystal lattice, those phonons which conserve the momentum participate for indirect transitions.

As a result of such considerations, gallium arsenide and other direct band gap semiconductors are used to make optical devices such as LEDs and semiconductor lasers, whereas silicon, which is an indirect band gap semiconductor, is not. The table in the next section lists a number of different semiconducting compounds and their band gaps, and it also specifies whether their band gaps are direct or indirect. Recent first principle calculations using DFT shows some indirect band gap materials are promising for photovoltaic applications (J. Kangsabanic et al, *J. Am. Chem. Soc.* 2022, 144, 43, 19872–19883, <https://pubs.acs.org/doi/10.1021/jacs.2c07567>)

	Material	Direct / Indirect Bandgap	Band Gap Energy at 300 K (eV)
Elements	C (diamond)	Indirect	5.47
	Ge	Indirect	0.66
	Si	Indirect	1.12
	Sn (grey)	Direct	0.08
Groups III-V compounds	GaAs	Direct	1.42
	InAs	Direct	0.36
	InSb	Direct	0.17
	GaP	Indirect	2.26
	GaN	Direct	3.36
	InN	Direct	0.70
Groups IV-IV compounds	$\alpha$ -SiC	Indirect	2.99
Groups II-VI compounds	ZnO	Direct	3.35
	CdSe	Direct	1.70
	ZnS	Direct	3.68

Data from R.E. Hummel, Electronic Properties of Materials, 3rd edition, Appendix 4, p. 413.

### Uv-Vis spectroscopy for optical band gap measurement:

Uv-Vis spectroscopy which measures light absorption as function of wavelength gives information on electronic transitions occurring in semiconductor material as function of incident light wavelength thus acts as a tool to estimate the optical band gap. Optical band gap is approximated to electronic band gap which is defined as energy difference between conduction band minimum and valence band maximum.

as per the Beer-Lambert law,

$I_T = I_0 e^{-\alpha d}$ , where  $\alpha$  is absorption coefficient and 'd' is the thickness of the sample. ' $I_T$ ' is the transmitted light and ' $I_0$ ' is the incident light.

The absorption coefficient  $\alpha$  is given by

$$\alpha(\text{cm}^{-1}) = \frac{2.303 A}{d}$$

Where A is absorbance which is defined as  $\log_{10}(I_0/I_T)$

Energy band gap of a given material can be precisely calculated using Tauc method as given below.  $\alpha = C [h\nu - E_g]^n$ .  $n = \frac{1}{2}$  for direct allowed transitions and  $n=2$  for indirect allowed transitions. For complete derivation of this formula refer to Book by J.A.Pankove, Optical processes in Semiconductors, Dover publications, 1971

Therefore, for direct band gap materials,

$$\alpha = C [h\nu - E_g]^{0.5}$$

Direct band gap materials also exhibit sharp rise in absorption above the  $E_g$  in the plot of energy of light source of Uv-vis setup versus absorption coefficient  $\alpha$

For indirect band gap materials,

$$\alpha = C [h\nu - E_g \mp E_p]^2$$

In the above equation for indirect band gap, '-' sign corresponds to phonon absorption and '+' corresponds to phonon emission. Phonon absorption and emissions are shown in Fig.1. But in some of the cases, phonon absorption and emission are not clearly seen in the indirect band gap data. In this case,  $\sqrt{\alpha}$  is plotted versus energy and then by the intercept of the linear region, band gap is estimated.

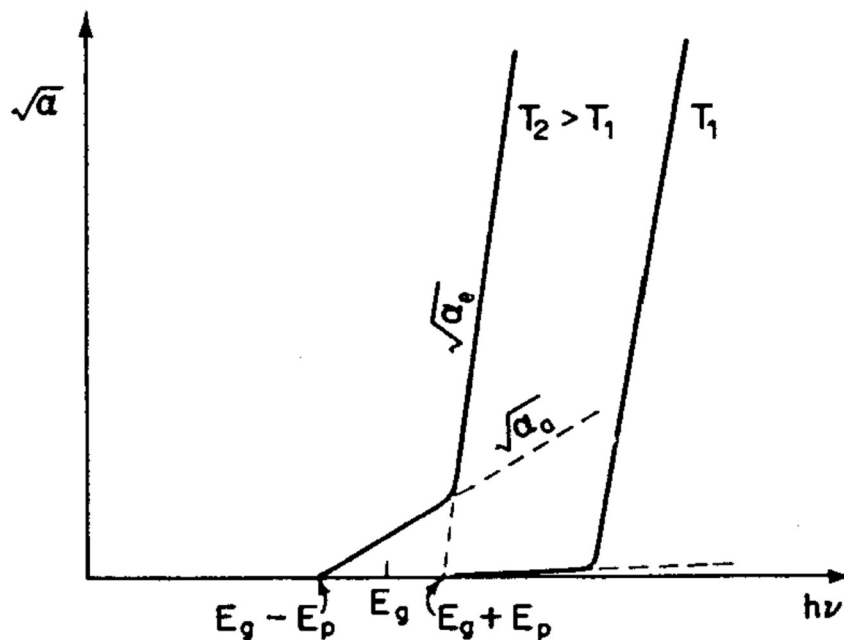


Fig.1 Representative plot energy versus  $\sqrt{\alpha}$  of indirect band gap taken from "Optical processes in semiconductors book by J.I. Pankove" ( $\sqrt{\alpha}$  versus  $h\nu$  shows two

slopes at  $T_2$  temperature indicating the phonon emission and absorption characteristic to indirect band gap.)

Other electronics transitions such as transition between band and impurity level manifest as shoulder in the absorption data. Example of the same is given in the following figure which is for impurity absorption in InSb.

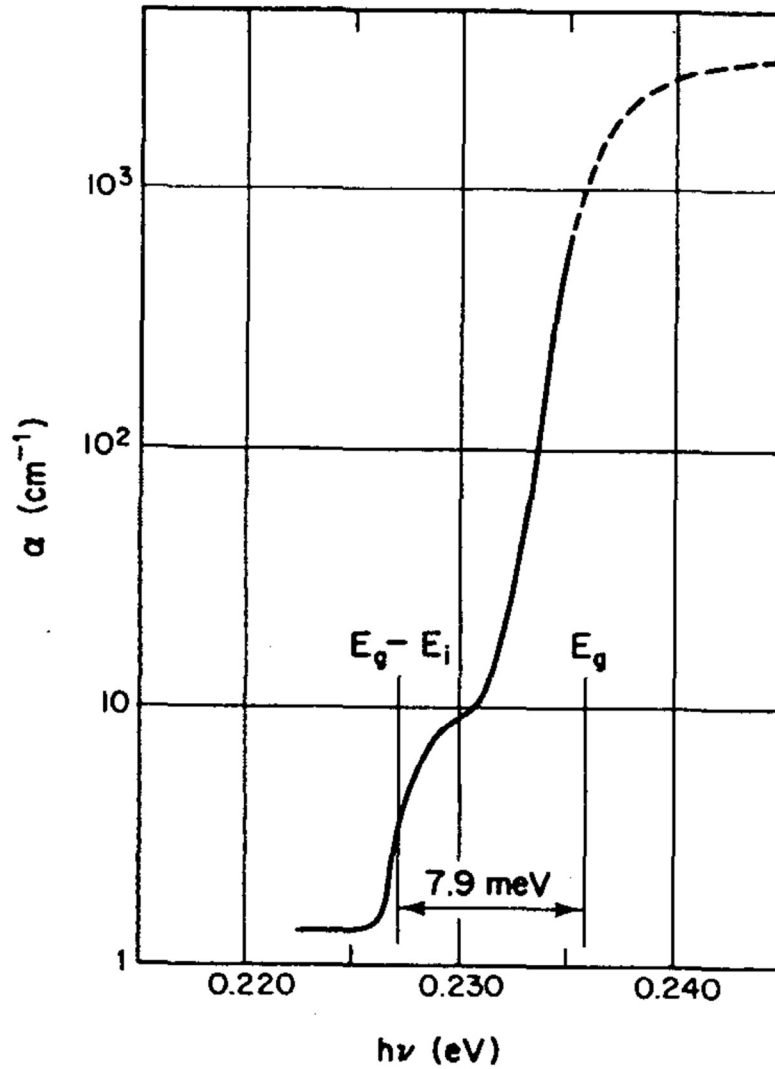


Fig.2. Energy versus absorption coefficient for InSb with impurity level absorption

### Procedure to collect Uv-Vis spectra and estimate the band gap:

1. Switch on the lamp wait for the lamp to warm up (5 minutes)
2. Switch on the computer and open the spectrum analyzer software. Keep averaging 5 and exposure 5 as first guess.
3. There are two thin film samples provided to you. Handle them by holding the edges, do not touch any of the glass slides face.
4. Open the sample holder unit. Insert the thin film sample deposited on glass slide with help of technician in the sample holder of spectrometer. Insert the position of the glass slide such that you should be able to take data on the glass and sample by using push pull knob of sample holder box. Close the sample holder unit with the lid.
5. First take the data of reference (empty area of the glass slide) by clicking the 'capture'. Maximum count of the detector is 65500. If the count is exceeding 60000, decrease the exposure and if it is less, increase the exposure. Finally, optimize both exposure and averaging.
6. To minimize the reflection and refraction during the measurement, keep the sample normal to the source of light.
7. Collect the reference data by clicking 'play' and then 'stop' after few seconds. If the data does not saturate, click 'Ref' and save this data as reference.
8. Switch off the lamp, without changing any settings, click 'play' and 'stop'. Save this data as dark data by pressing 'Dark' on the software.
9. Switch on the lamp and wait for a minute, by push pull knob adjust the position of the sample such that light falls on thin film. Then click 'capture' to see if the data is being collected for thin film
10. Finally, click start and stop. Click absorbance knob on the side panel to view the absorbance.
11. Export the data to an excel file by clicking export and save the file with your name and sample details.
12. Convert the wavelength to energy in eV and calculate absorption coefficient( $\alpha$ ) from absorption.
13. Plot  $\alpha$  vs energy,  $\alpha^2$  vs energy and  $\sqrt{\alpha}$  vs energy. Direct band gap material shows high absorption and sharp rise in  $\alpha^2$  vs energy. Identify the linear region and select the region and fit it to straight line to find intercept to estimate band gap. Observe in this case that  $\sqrt{\alpha}$  vs energy does not show any meaningful linear region for the samples given.
14. For indirect band gap you are given the data of Si based material collected in research lab of Uv-Vis spectrometer. It has a shoulder in the absorbance data which is due to impurity similar to Fig.2, therefore, consider the data only after 1.2 eV, identify linear regions in  $\sqrt{\alpha}$  vs energy and fit the straight line to the identified data. Using the intercept of best fit line, estimate band gap energy.

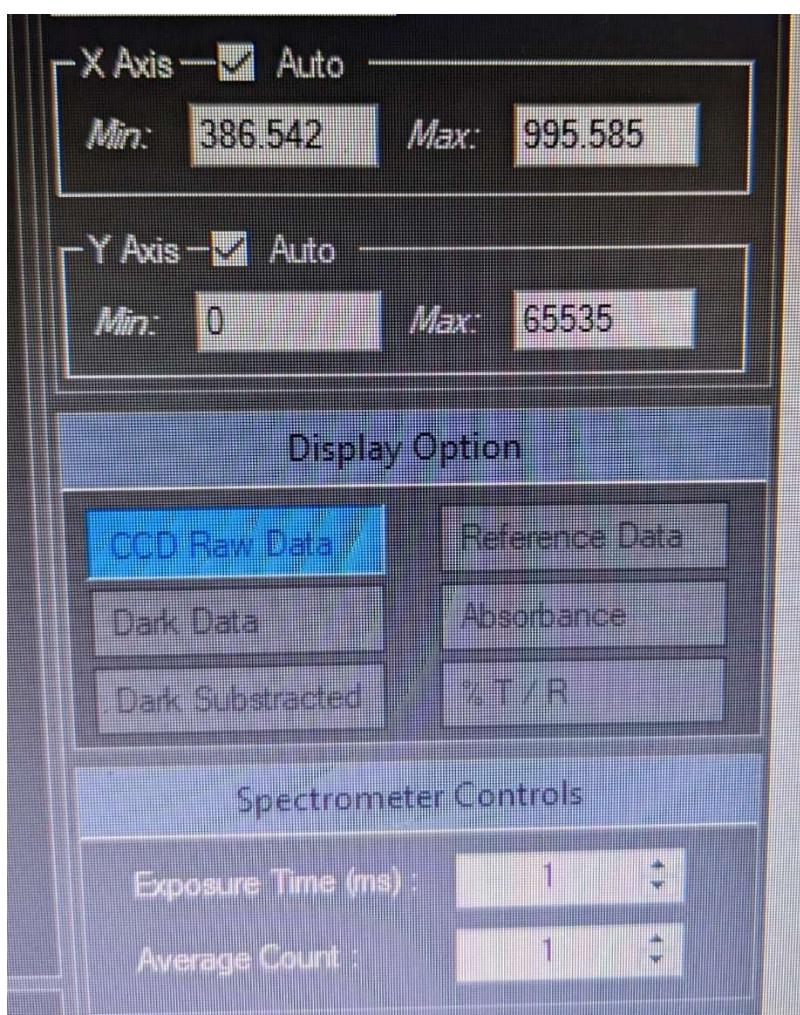
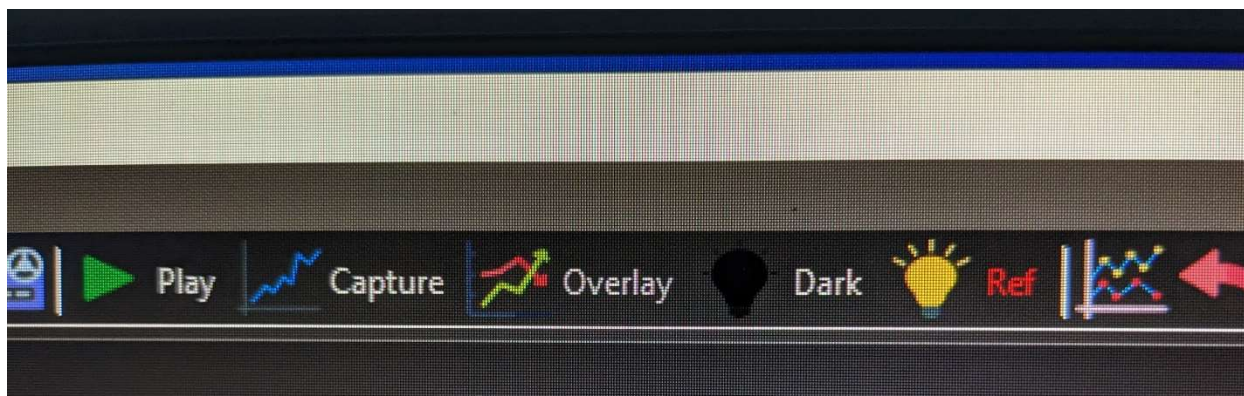


Fig.3a and 3b: Snapshots of the software screen for Uv-Vis spectrometer.

## References:

1. <https://www.doitpoms.ac.uk/tlplib/semiconductors/direct.php>
2. [https://en.wikipedia.org/wiki/Direct\\_and\\_indirect\\_band\\_gaps](https://en.wikipedia.org/wiki/Direct_and_indirect_band_gaps)
3. <https://mmrc.caltech.edu/Cary%20UV-Vis%20Int.Sphere/Literature/Spectroscopy%20Jaramillo.pdf>
4. J.A.Pankove, Optical processes in Semiconductors, Dover publications, 1971
5. A. R. Zanatta, Scientific Reports volume 9, Article number: 11225 (2019)
6. <https://www.nature.com/articles/s41598-019-47670-y>
7. <https://advlabs.aapt.org/document/ServeFile.cfm?ID=7815&DocID=632>