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18PYB103J –Semiconductor Physics

Determination of band gap by Uv-Vis spectroscopy

The measurement of the band gap of materials is important in the semiconductor, nanomaterial and solar industries. This note demonstrates how the band gap of a material can be determined from its UV absorption spectrum.
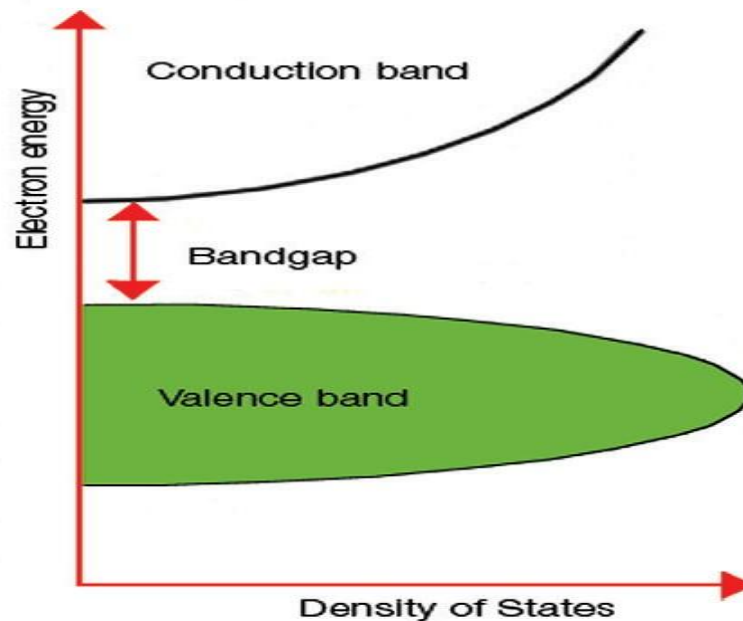
Figure 1. Explanation of band gap.

The term "band gap" refers to the energy difference between the top of the valence band to the bottom of the conduction band (See Figure 1); electrons are able to jump from one band to another.

In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition, the band gap energy.

A diagram illustrating the band gap is shown in Figure 1.

Measuring the band gap is important in the semiconductor and nanomaterial industries.

The band gap energy of insulators is large (> 4eV), but lower for semiconductors (< 3eV).

The band gap properties of a semiconductor can be controlled by using different semiconductor alloys such as GaAlAs, InGaAs, and InAlAs [1].

1.Jayant Dharma, PerkinElmer Technical Center, Aniruddha Pisal, Global Application Laboratory, PerkinElmer, Inc., Shelton, CT USA. file:///C:/Users/intel/Desktop/APP_UVVISNIRMeasureBandGapEnergyValue.pdf

A **Tauc plot** is used to determine the optical band gap, or Tauc gap, in semiconductors.

The Tauc gap is often used to characterize practical optical properties of amorphous materials. While investigating the optical and electronic properties of amorphous germanium, Tauc et al, proposed and substantiated a method for determining the band gap using optical absorbance data plotted appropriately with respect to energy [2].

This was further developed in Davis and Mott's more general work on amorphous semiconductors [3,4]. They show that the optical absorption strength depends on the difference between the photon energy and the band gap as shown in (Eq. 1):

$$(\alpha \hbar v)^{1/n} = A(\hbar v - Eg) \ (1)$$

where h is Planck's constant, v is the photon's frequency, α is the absorption coefficient, E_g is the band gap and A is a proportionality constant.

2.Tauc, J., R. Grigorovici and A. Vancu, *Optical properties and electronic structure of amorphous germanium. Physica Status Solidi, 1966.* **15**: *p. 627-637.*
3.Davis, E.A. and N.F. Mott, *Conduction in non-crystalline systems V. Conductivity, optical absorption and photoconductivity in amorphous semiconductors. Philosophical Magazine, 1970.* **22**: *p. 903.*
4.Mott, N.F. and E.A. Davis, *Electronic processes in non-crystalline materials. 2nd ed. 1979: Clarendon Press (Oxford and New York).*

The value of the exponent denotes the nature of the electronic transition, whether allowed or forbidden and whether direct or indirect:

For direct allowed transitions   n=1/2

For direct forbidden transitions n=3/2

For indirect allowed transitions n=2

For indirect forbidden transitions   n=3

Typically, the allowed transitions dominate the basic absorption processes, giving either n=1/2 or n=2, for direct and indirect transitions, respectively.

The resulting plot has a distinct linear regime which denotes the onset of absorption. Thus, extrapolating this linear region to the abscissa yields the energy of the optical band gap of the material.

Tauc plot
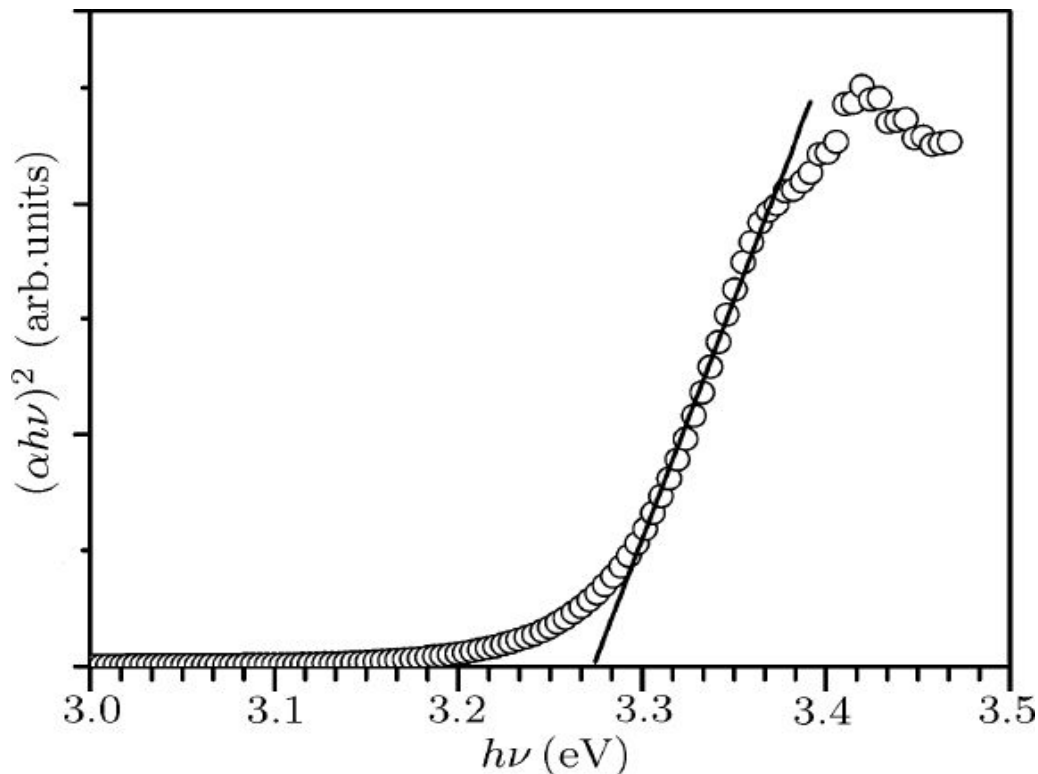
Figure 2: Example Tauc Plot from UV-Vis analysis of a ZnO thin film that illustrates the method of fitting the linear region to evaluate the band-gap at the X-axis intercept, here about 3.27 eV [5].

5.Wang, M.D., D.Y. Zhu, Y. Liu, L. Zhang, C.X. Zheng, Z.H. He, D.H. Chen and L.S. Wen, Determination of thickness and optical constants of ZnO thin films prepared by filtered cathode vacuum arc deposition. Chinese Physics Letters, 2008. **25**(2): p. 743-746.

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Figure 2 gives one example Tauc plot for ZnO where the absorption coefficient times the photon energy to the second power is plotted versus the incident photon energy[4].

The second power was used as zinc oxide is well known to have a direct allowed transition.

The characteristic features of Tauc plots are evident:

•   at low photon energies the absorption approaches zero – the material is transparent;

•   near the band gap value the absorption gets stronger and shows a region of linearity in this squared-exponent plot.

•   This linear region has been used to extrapolate to the X-axis intercept to find the band gap value (here about 3.27 eV).

•   At even higher energies the absorption processes saturate and the curve again deviates from linear.

To select and justify a linear region for extrapolation one must understand the reasons for these lower and upper deviations from linear behavior.

- On the low energy end, the deviation from linearity can be associated with defect absorption states that are near the band edge. This phenomenon has been investigated by Urbach [6] and in subsequent years, therefore, identified as an "Urbach Tail." These states are usually described by an exponential function, corresponding to a typical distribution of density of states, evident in the absorption behavior seen in the example Tauc plot (Figure 2).

- On the high energy end, saturation of available transition states is responsible for a leveling out of absorption strength in most collected spectra [7].

6.Urbach, F., The Long-Wavelength Edge of Photographic Sensitivity and of the Electronic Absorption of Solids. Physical Review 1953. 92: p. 1324.

7.Brian D. Viezbicke., Shane Patel., Benjamin E. Davis, and Dunbar P. Birnie, III., Evaluation of the Tauc Method for Optical Absorption Edge Determination: ZnO Thin Films as a Model System. Physica Status Solidi, B 2015 252(8), 1700-1710.

Concept of Photoluminescence

- Luminescence is an electromagnetic (EM) radiation phenomenon due to excessive thermal radiation or incandescence in physical system.

- With regard to luminescent semiconductors, when energy of incident photon is equal or beyond the energy band gap, it will excite the electron of valence band into conduction band through band gap.

- Semiconductors generate recombination radiation from excited state to ground state.

- Absorption will also happen when an electron is excited to higher energy level from neutral acceptor energy level and it can also transit to ionization donor energy level from valence band or transit to conduction band from ionization acceptor energy level. Those phenomena can explain the energy band or impurities in the semiconductor successfully.
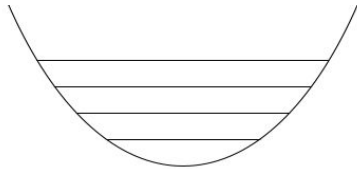
Concept of Photoluminescence

• Photoluminescence which inspects optical property of luminescent semiconductor materials is a strong and nondestructive technology.

• According to analytic data of photoluminescence, we can know the kind of impurities, band gap, and impurity activation energy etcetera from the spectra.

• We can estimate the composition of the compound from the peak intensity of PL spectra.

• Using photoluminescence can investigate the internal interface of hetero-structure that general physical or electronic measurements can not measure.
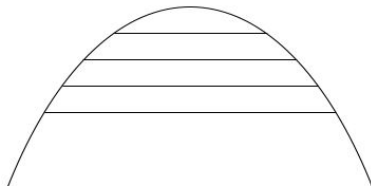
Fluorescent solutions under UV-light. Absorbed photons are rapidly re-emitted under longer electromagnetic wavelengths.

Concept of Photoluminescence

• Luminescence process includes three procedures: (1) Excitement, (2) Heat balance, (3) Recombination.

• Incident light generates electron-hole pairs and recombines to generate photons after heat balance.

• Impurities and defects form various energy levels in the band gap and their corresponding energy will generate radiation by radiation recombination process or generate absorption by non-radiation recombination process.

Schematic for the excitation-relaxation processes of photoluminescence.

Luminescence of semiconductors can divide two types:

(1) Radiative transition

When an electron drops to lower energy state from higher energy state, it will probably occur radiative transition regardless of intrinsic state or energy state formed by impurities. Therefore, the system is not a balanceable condition and we assume that excited phenomena will generate electron-hole pairs in semiconductors. Firstly, we consider some basic transitions:

(a)Band-to-band transition:

Band-to-band transition is the relationship of free-electrons and holes. Those transitions usually occur in direct band gap materials such as Ⅲ-Ⅴ compounds where the electron-hole pairs will generate radiation recombination effectively between conduction band and valence band.

Concept of Photoluminescence

(b)Free exciton transition

If the material is very pure, an electron and a hole will attract each other to form exciton. Then, they will recombine to generate a very narrow spectrum. In Ⅲ-Ⅴ compounds, free exciton energy state usually describes Wannier-Mott approximation. The energy of free exciton can be expressed as Equation 1.

$$E_n = 2\pi^2 m^* e^4 / h^2 \varepsilon^2 n^2 \qquad (1)$$

In this equation, m* is effective mass, h is Planck constant, ε is dielectric constant, and n is quantum number.

However, there are probably several mechanisms to result in non-radiative transition. Those transitions will compete with radiative transition to result in lower luminescence.

Concept of Photoluminescence

(c) Free-to-bound transition

The transition is free-to-bound transition between energy bands of materials and impurity energy level. This transition is between the impurity and one of energy bands such as from conduction band to acceptor or from donor to valence band. The energy of radiative photon is $E_g - E_b$ and E_b is bound energy of shallow impurity energy level.

(d) Donor-acceptor pair recombination

The transition is between donor and acceptor. After optical pumping, the electrons and holes will be bounded at D+ and A- locations to generate neutral D_0 and A_0 centers. Some neutral donor electrons will recombine with neutral acceptor holes radiatively.

Concept of Photoluminescence

Non-radiative transition

Some opportunities which cause non-radiative transition will compete with radiative recombination transition and influence luminescent efficiency negatively. They can describe as below:

a) Because of thermal oscillation to generate phonons;

b) Recombination on the surface state includes two dimensional dislocation, and agglomerative boundary et al. through step-wise transition which causes loss energy. It also calls cascade process;

c) Impurity locations are often not radiative recombination centers;

d) Loss energy of trapped carriers will excite other carriers in the lattice and emit non-radiative loss energy by Auger process.