Method of measurement of energy gaps in semiconductor

Kapila P Hewaparakrama

Department of Physics
University of Cincinnati
Cincinnati, Ohio 45221

June 4,2001

Abstract

This paper presents a particular experimental method to determine the band gaps of Semiconductors through the optical absorption spectra. The procedure of analysis of the spectra is discussed for two cases, i.e for direct and indirect band gaps. Two examples of experimental results have been presented. It is shown that $SrTiO_3$ has an indirect band energy of 3.16 eV at 10 K and the direct band gap of CdTe thin film decreases with the increasing thickness.

1 Introduction

Characteristic of semiconducting and insulating material is a band gap between valence and conduction bands.The Energy band gap of a semiconductor material plays an important role in determining the photo-conversion efficiency of a solar cell. There are many methods to determine the energy band gaps namely optical absorption method, photoelectrochemical methods, intrinsic conduction measurement at high temperature, photoemission and band structure calculation. Here, optical absorption method is used to determine the energy band gaps of semiconductor.

1.1 Absorption of Light in Semiconductor

When incident photon energy exceeds the band gap of a semiconductor, electrons can be excited from the valence to the conduction band. Removal of an electron from the valence band creates a positively charged vacancy called a hole. The light passing through the material is absorbed then, and the number of generated electron-hole pairs depends on the number of incident photons $\Gamma_0(\nu)$ (per unit area, unit time and unit energy). Inside the semiconductor, the photon flux at position x ,$\Gamma(x,\nu)$, can be expressed as a function of absorption coefficient $\alpha(\nu)$,

$$\Gamma(x,\nu) = \Gamma_0(\nu)exp(-\alpha x) \tag{1}$$

The abosption coefficient $\alpha(\nu)$ depends on the band structure of the semiconductor.There are two major processes of absorption involved in determining α, they are called direct and indirect absorptions.

1.2 Direct and Indirect band gaps in semiconductor

In the semiconductors, the band gap can be classified as direct or indirect -a band gap is said to be “direct” when the energy minimum (the bottom) of the conduction band lies directly above the energy maximum (the top) of the valence band in reciprocal k-space (Fig. 1a) Otherwise, we call it an “indirect” band gap (Fig. 1b).
At the top of the valence band and at the bottom of the conduction band have the same wave vector in a direct band gap solid, but different wave vectors in an indirect band gap material. Whether the gap is direct or indirect is important in the application of inorganic semiconductors (such as Si, Ge and GaAs) to photoconduction and electroluminescence[1]
.

1.2.1 Direct Optical Absorption in semiconductor

The direct optical absorption process is illustrated in Fig. 1a. It is a first order process involving only the absorbed photon, which can be represented approximately as a vertical line on energy vs. wave vector plot(K). If $h\nu$ is the photon energy and ΔE is the energy gap of the semiconductor.Then

$$\Delta E = h\nu \tag{2}$$

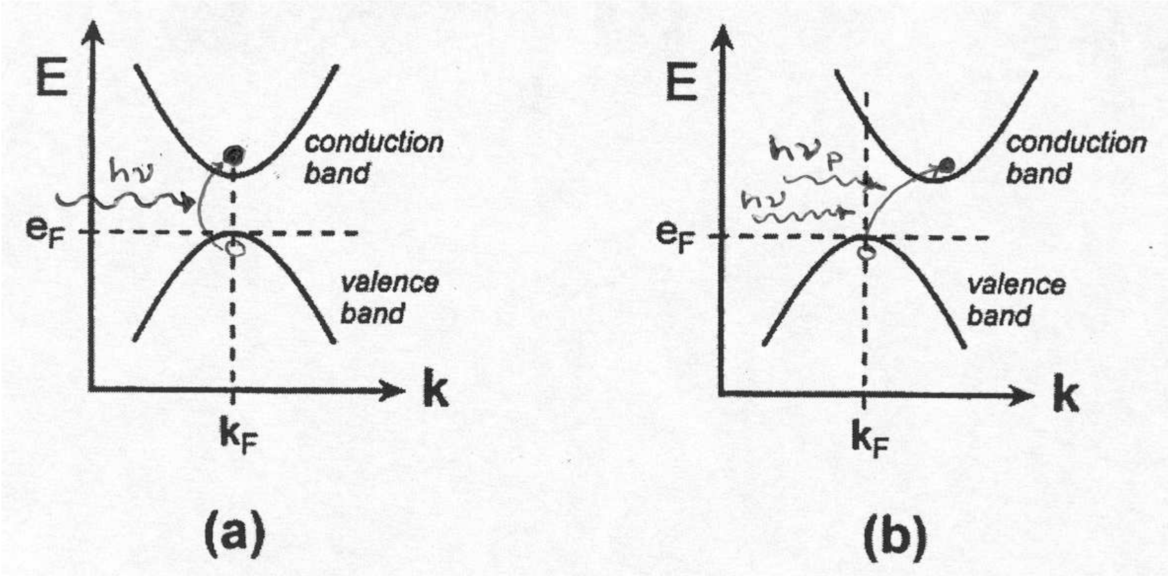

Figure 1: *Schematic representations of electronic band structures near the Fermi level for (a) a semiconductor with direct band gap and (b) a semiconductor with n indirect band gap. ϵ_F is the Fermi level having the Fermi wave vector K_F.[1]*

The expected variation of α with photon energy near the minimum energy for absorption E_g^d is given by

$$\alpha(h\nu) \;=\; c(h\nu - E_g^d)^{1/2} \tag{3}$$

where c is a constant.
Therfore a plot of α^2 as a function of photon Energy $(h\nu)$ yields a straight line for a direct absorption(fig. 2a). Direct Energy band gap can be obtained from that plot.

1.2.2 Indirect Optical Absorption in semiconductor

An indirect optical absorption process is illustrated in Fig 1b. It is a second order process involving both the absorbed photon and a simultaneously absorbed or emitted phonon, which occurs when the minimum of the conduction band and the maximum of the valence band occur at different values of wave vector K. The absorption transition conserves energy

$$\Delta E \;=\; h\nu \pm E_p \tag{4}$$

where $h\nu$ is the photon energy and E_p is the phonon energy. The absorption-edge of the indirect gap is well described by[6]

$$\alpha(h\nu) \;=\; A\left[\frac{(h\nu - h\nu_p - E_g^i)^2}{1 - \exp^{-E_p/KT}} + \frac{(h\nu + h\nu_p - E_g^i)^2}{\exp^{E_p/KT} - 1}\right] \tag{5}$$

where A is a constant, K is the Boltzmann constant,$h\nu_p(= E_p)$ is the phonon energy participating in the transition, and E_g^i is an indirect band gap energy. A plot of $\alpha^{1/2}$ as a function of photon Energy $h\nu$ gives the two values at $\alpha^{1/2}$=0 from the two dotted straight lines as shown in the fig.2b. Then, indirect band gap of the semiconductor is

$$E_g^i = \frac{E_1 + E_2}{2} \tag{6}$$

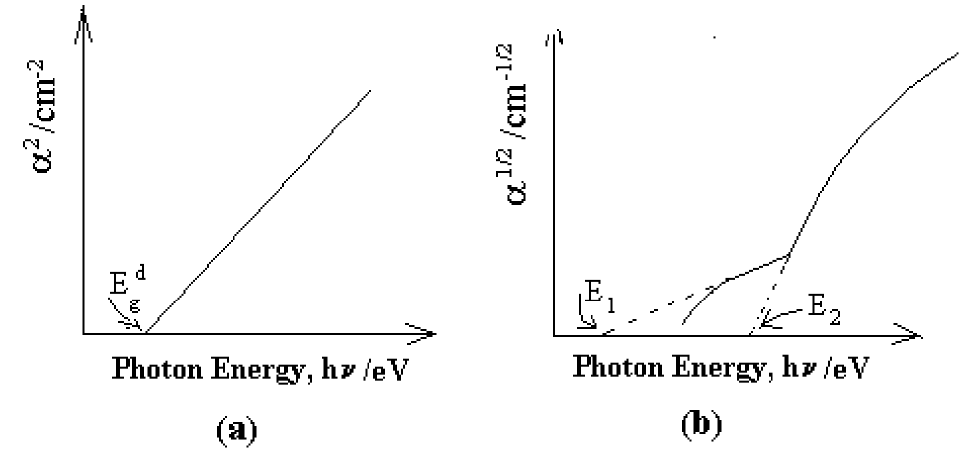

Figure 2: *The graph of the (a)α^2 versus photon energy for direct band gap semiconductor and (b) $\alpha^{1/2}$ versus photon energy verses for indirect band gap semiconductor.[2]*

2 Experimental set-up

The essential components of a spectrophotometer include: (1) a stable source of radiant energy, (2) a monochomator to resolve the radiation into component wavelengths or bands of wavelengths, (3)sample compartment and (4) a radiation detector.

2.1 Sources of Radiation

A tungsten filament lamp is the most satisfactory and inexpensive source of visible and infrared radiation. The filament is heated by a stabilized d-c power supply, or by a storage battery. The tungsten filament emits continuous radiation in the region between 350 nm and 2500 nm. For source of ultraviolet radiation, the hydrogen lamp and deuterium lamp are used. They consist of a pair of electrodes which are enclosed in a glass tube provided with a quartz window and filled with hydrogen or deuterium gas at low pressure. When a stabilized high voltage is applied to the electrodes, an electron discharge occurs which excites other electrons in the gas molecules to high energy states. As the electrons return to their ground state they emit radiation which is continuous in the region roughly between

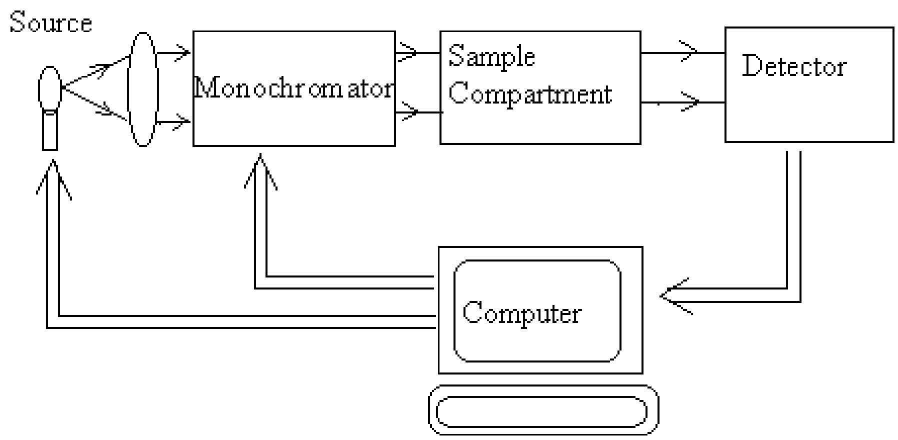

Figure 3: *Block diagram of absorption apparatus.[3]*

180 nmand 350 nm. Similarly, a xenon discharge lamp is used as a source of ultraviolet radiation. The xenon lamp produces higher intensity radiation, but it is not as stable as the hydrogen lamp. It also emits visible radiation which may appear as stray radiation in ultraviolet applications.[3]

2.2 Monochromators

The souces of radiation commonly used emit continuous radiation over wide ranges of wavelengths. However, narrow band widths have many advantages: (1) narrow band radiation will allow the resolution of absorption bands which are quite close to each other,(2) with narrow band radiation a peak may be measured at its absorption maximum, thus increasing the sensitivity, and (3) the absorption of narrow band radiation will tend to show greater adherence to Beer's law because only that radiation which can be absorbed is measured. Monocromators resolve wide band polychromatic radiation from the source into narrow bands or monochromatic radiation with effective band widths varying from 35 $m\mu$ to 0.1 $m\mu$. The components of monochromator include: (1) an entrance slit which admits polychromatic radiation from source; (2) a collimating device, either a lens or a mirror; (3) a dispersion device, either a prism or grating, which resolves the radiation into component wavelengths; (4) a focusing lens or mirror; and (5) an exit slit. The effective band width of radiation emerging from the monochromator depends on several factors, including the dispersing element and the slit widths of both the entrance and exits slits. Narrow slit widths isolate narrow bands; however, the slit width also limits the radiant power which reaches the detector. Therefore, the minimum band width may be determined by the sensitivity of the detector.[3]

2.3 Detection Devices

Any detector absorbs the energy of the photons which strike it and converts this energy to a measurable quantity such as the darkening of a photographic plate ,an electric current,or thermal changes. Most modern detectors generates an electrical signal. Any detector must generate a signal which is quantitatively related to the radiant power striking it. The noise of a detector refers to the background signal generated when no radiant power from the sample reaches the detector. This noise may be caused either by random changes within the detector itself or by electrical pick up of other signals in the vicinity of the detector unit. Important requirements for detectors include: (1) high sensitivity with a low noise level in order to allow the detection of low levels of radiant power, (2) short response time,(3) long term stability to insure quantitative response, and (4) an electronic signal which is easily amplified for typical readout apparatus. and exits slits. Narrow slit widths isolate narrow bands; however, the slit width also limits the radiant power which reaches the detector. Therefore, the minimum band width may be determined by the sensitivity.[3]

2.3.1 Ultraviolet and Visible Radiation Detectors

Ultraviolet and Visible photons possess enough energy to cause photoejection of electrons when they strike surfaces which have been treated with specific types of compounds. Their absorption may also cause bound, non-conducting electrons to move into conduction bands in certain semiconductors. Both processes generate an electric current which is directly propotional to the radient power of the absorbed photons. Device which employ these systems are called photoelectric detectors and are sub-classified as phototubes and photovoltaic cells.[3]

2.4 General Procedure of Measurement and Analysis

In principle we want to detect the spectrum that comes purely from the sample. In practice, however we cannot avoid of having the spectrum of our sample get mixed with that from other sources such as from the substrate, or from some noice existing in the sample compartment. We therefore need to do two measurements, one without the sample and the other one with the sample. The spectrum, namely the quantity $\Gamma(\nu, x)$, that we will analyze is then the difference between $\Gamma(\nu, x)$ without sample and $\Gamma(\nu, x)$ with the sample. In the analysis we extract $\alpha(\nu)$ from $\Gamma(\nu, x)$ by means of equation (1). $\alpha(h\nu)$ is the plotted against $h\nu$. Finally by looking at the graphs and refering to equation (3) (for direct gap) or equation(5) (for indirect gap) we can extract the value of E_g.

3 Examples of experimental results.

From the absorption mesurements above 77 K, it is reported that $SrTiO_3$ has an indirect band gap[4] in accordance with the band calculation[5]. Fig.4 shows absorption-edge spectra in the square-root scale. A simple linear shape at 10-60 K indicates that $\alpha(h\nu)$ has a quadratic dependance on the phonon energy, which means that $SrTiO_3$ has an indirect band gap.The absorption edge of the indirect gap is well discribed by eq.(5).Experimental results are well reproduced by eq.(5) with $E_g^i = 3.16eV$.

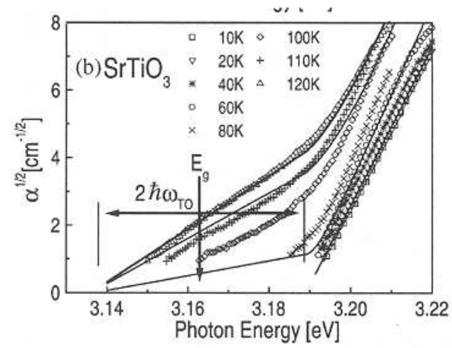

Figure 4: $\alpha(h\nu)$ *is plotted in the square-root scale below 120 K. Solid line shows the calculated curves at 10,60,110,120 K using eq.(2).[6]*

The $(\alpha h\nu)^2$ versus $h\nu$ plots for CdTe films of different thicknesses but deposited at identical conditions are shown in Fig.5. It has been observed that the direct band gap decreases with increasing thickness.[7]

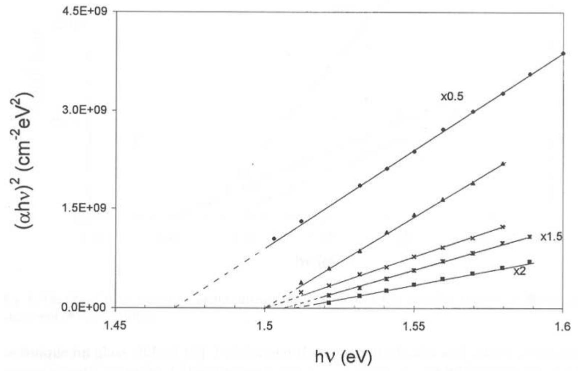

Figure 5: *Plot of* $\alpha(h\nu)^{1/2}$ *vs.* $h\nu$ *for CdTe films of different thicknesses.[7]*

References

[1] Dong-Kyun Seo, R. Hoffmann , T̈heoritical Chemistry Accounts 102(1999) 23.

[2] N.B.Hannay,S̈emiconductor 443(1959)

[3] H.H.Willard,L.L.Merritt, ÏNSTRUMENTAL METHODS OF ANALYSIS.

[4] M.Capizzi, A.Frova,P̈hys.Rev.Lett. 25(1970) 1298.

[5] A.H.Kahn, A.J.Leyendecker,P̈hys. Rev.135(1994)A1321.

[6] T.Hasegawa, M.Shirai, K.Tanaka,J̈ournal of Luminescence 87(2000)1217.

[7] X.Mathew, P.J.Sebbastian, S̈olar Energy Materials and Solar Cells 59(1999)85. 43(2000)66.