OPTICAL ABSORPTION EDGE OF SEMICONDUCTORS

1. References

C. Kittel, "Introduction to Solid State Physics" 7th edition (1996)

R. A. Smith, "Semiconductors," Cambridge University Press (1961)

T. P. McLean, J . E. Quarrington, and V. Roberts, Phys. Rev. 108, 1371 (1957) and

111, 1245 (1958).

F. Wooten, "Optical Properties of Solids," Academic Press (1972)

J. I. Pankove, "Optical Processes in Semiconductors," Dover Publications, N. Y. (1972).

The book by Jacques I. Pankove is particularly good (inexpensive Dover paperback). It introduces you to the band structure of semiconductors, the fundamental absorption processes in direct and indirect band gap semiconductors, and the relationships between optical constants.

2. Purpose

To measure the energy gap, refractive index and attenuation coefficient of Si, Ge and GaAs.

3. Introduction

Semiconductors like silicon (Si) and gallium arsenide (GaAs) constitute the most controllable quantum many-body system available to physics. Since their perfection in the 1980's these semiconductors have revealed numerous new collective quantum-coherent phenomena, such as the fraction quantum Hall Effect recognized by the Nobel Prize of 1998. The controllability of single electron states in silicon via transistors is responsible for their dominance in information processing and control in practical life. This laboratory reveals these states directly and suggests the factors controlling them. The chief feature of interest is the famous energy gap: in order to create an electronic excitation in a semiconductor, a non-zero threshold energy is required. The manipulation

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of this threshold and the number of available excited states above it provide the principal means of controlling electron flow used in transistors and other devices.

A polished surface of many semiconductors has the characteristic luster of polished metals. The reason for this is their high reflectivity. In the visible region of the spectrum, semiconductors absorb strongly like metals, having coefficients of absorption of the order of $\alpha \approx 10^5$ cm^{-1}. The coefficient α depends on the photon frequency f or equivalently its energy hf where h is Planck's constant.

The absorption coefficient is defined according to,

$$I' = I_i e^{-\alpha d} \tag{1}$$

where I_i is the initial intensity of the light and I' is the intensity after traveling a distance d through a material with absorption coefficient α.

As one decreases the photon energy (increases the wavelength) toward the infrared, one observes a sudden drop in absorption followed by a spectral region in which semiconductors are transparent. This "fundamental absorption edge" lies at a photon energy which is just sufficient to excite electrons across the energy gap E_g which separates the highest band of states occupied by electrons (valence band) from the next band of states (conduction band) which is unoccupied by electrons at the temperature of absolute zero. The magnitude of the gap which ranges from 0.17 eV in InSb to 12 eV in LiF is, of course, an important factor determining the optical, electrical, and photoelectrical properties.

In this experiment you will determine the band gap energy E_g for GaAs, Si, and Ge semiconductors from measurements of $\alpha(hf)$ through the optical absorption edge.

In the simplest picture, light quanta above the band gap energy create electronic excitation in the semiconductor, whereas quanta below this energy do not. This creates a readily observable decrease in transmission through the sample as the light frequency increases. By viewing the process in more detail, one may learn several other important features of the electronic excitation as

detailed below. One must also cope with some subtleties in inferring the electronic properties from the observed changes in transmission.

The basic quantum mechanics governing the rate at which an initial-state photon is converted into electronic excitation is the same as that for ionization of an atom. The governing equation is *Fermi's Golden Rule* treated in all quantum mechanics texts. For any given initial state, the rate is proportional to the square of a matrix element times the sum over available final states that conserve energy. In an atom, the final state consists of a free electron and the ion, i.e., the initial atom with a missing electron. In a semiconductor the simplest final states consist of a propagating electron and a missing electron in a formerly occupied state. Such missing electrons are known as holes. Thus the rate of absorption of the initial photon is proportional to the number of electron-hole states having the energy of the initial photon. This energy is basically the sum of the electron's energy and the hole's energy. If the energy lies below the gap energy there are no such states in the simplest picture, and the absorption rate is zero. As the energy rises above the gap, the number of final states increases in a calculable way.

There is a restriction on the allowed final states: translational symmetry in the semiconductor means that there is a conserved wave-vector variable denoted k. The electrons have wavelengths of the order of a few Angstroms--a few times the spacing between the atoms. The incident photons with energies of interest have much longer wavelengths of order 10^4 Angstroms. For our purposes the photon's wave-vector (inverse wavelength) is negligible. In order to conserve the wave-vector variable, the wave-vectors of the excited electron and hole must thus add up to zero. Using these facts, one many compute how the number of final states increases with energy. These formulas are derived in Kittel's text cited above.

Thermal excitations modify the above picture. Because of these, the initial state is not the ground state of the semiconductor. In particular, vibrational modes are excited. These modes have energies of order k_BT, about 1/40 eV at room temperature. To account for such excitations, one must average over the thermally excited initial states. Final states may also have vibrational modes

in addition to the electron and hole. The discussion below explains how these vibrations affect the absorption.

GaAs: is a ***direct band gap*** semiconductor. Hence for allowed direct optical transitions between the occupied valence band and the empty conduction band one obtains (Pankove p. 36):

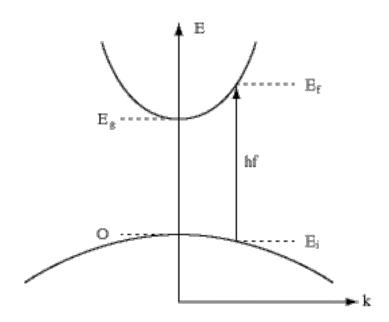$$\alpha(hf) = A(hf - E_g)^{1/2} \tag{2}$$

Fig. 1 Bands near a direct gap, after Pankove, p. 35

This square root dependence reflects the density of final states, consisting of one electron added to the upper band and one hole removed from the lower one.

Si and Ge: are ***indirect band gap*** semiconductors; that is, their highest occupied electronic state has a different wavevector than their lowest empty state. Optical transitions from the valence to the conduction band can occur only if a phonon is emitted or absorbed at the same time. Moreover, the phonon must have a wavevector about equal to the difference in wavevector of the two bands. If the phonon has the energy E_p then the absorption coefficient with phonon absorption is for

$hf > E_g - E_p$:

$$\alpha_a(hf) = A \frac{\left(hf - E_g + E_p\right)^2}{e^{\left(E_p/kT\right)} - 1} \tag{3}$$

and with phonon emission for $hf > E_g + E_p$ is

$$\alpha_e(hf) = A \frac{\left(hf - E_g - E_p\right)^2}{1 - e^{\left(-E_p/kT\right)}} \tag{4}$$

(Pankove p. 38). Here the numerator arises from the density of final states, each consisting of the state of the removed electron, the final electron and the phonon. The denominator tells the number of phonons present in thermal equilibrium. In eq.(3), it tells the number of phonons available for absorption; in eq.(4) it tells the number of phonon states available for emission.

There is no clear distinction between semiconductors and insulators but roughly speaking, materials having energy gaps smaller than say 2.5 eV are considered semiconductors. Table 1 of Chapter 8 in Kittel's *Introduction to Solid State Physics* lists the energy gaps of a number of crystals. One notices that the energy gap increases (i) as the atoms connected by covalent bonds get smaller and hence can get closer together: Sn--Ge--Si--diamond, and (ii) as the ionicity of the bond increases: Ge--GaAs--ZnSe--KBr.

4.   Procedure

You will use a Beckman spectrophotometer to make measurements of the fraction of light transmitted through different semiconductor samples as a function of wavelength. This instrument uses a chopping technique to make alternating measurements of the intensity of the light with and without a sample in the optical path. The ratio of the two intensities is used to determine the fractional transmission T of the sample as defined in eq.(5).

$$T = \frac{I_i}{I_t}, \tag{5}$$

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where I_i is the intensity of the light in the absence of the sample and I_t is the intensity after passing through the sample.

A schematic of the instrument is shown in Figure 2. Light from the source (A) is focused on the slit (E) by the condensing mirror (B). The directed beam from the condensing mirror (B) is deflected through the chopper (D) and upon the entrance slit (E) by the slit entrance mirror (C). Light focused on the slit (E) falls on the collimating mirror (F) and is rendered parallel and reflected to the quartz prism (G). The back surface of the prism is aluminized so that light is reflected back through the prism. The desired wavelength of light is selected by rotating the wavelength selector which adjusts the angular position of the prism. The spectrum is directed back to the collimating mirror (F) which focuses the selected wavelength in the slit (E). Light leaving the monochronometer is focused by the lens (H) into the sample compartment, where the beam is alternately switched between the reference path (J) and the sample path (M) by rotating mirrors (I and N) and stationary mirrors (L and K). The beam entering the photocell compartment is focused by the spherical condensing mirror (O) on either the lead sulfide detector (P) or the photomultliplier detector (Q).
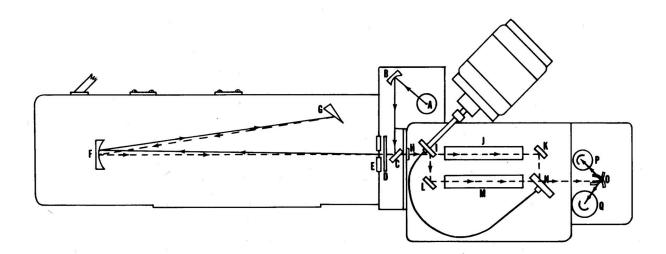

Figure 2. Optical path for Beckman Spectrophotometer.

In order to compensate for changes in measured intensity of the signal in the *Reference* channel, due to the spectral shape of the blackbody spectrum for example, the spectrophotometer uses a feedback circuit to control the width of the slit (E) so as to maintain constant intensity of the *Reference* signal. The ratio of the *Sample* signal to the *Reference* signal gives the fractional transmission of the sample.

This spectrophotometer was designed to scan automatically over a user-selectable wavelength range while plotting the data as % transmission vs. wavelength using the built in XY recorder. However, the speed of the scan is faster than the electronic and mechanical response time of the automatic slit control and you cannot obtain reliable measurements at the absorption edge where the transmission changes rapidly. To get around this limitation we have modified the apparatus so that the transmission output can be read as a voltage on a meter. You will take data by manually setting the wavelengths to be measured and recording the transmission data from the voltage output.

4.1   Calibrating the intensity

Before you begin to make measurements calibrate the spectrophotometer so that you are making use of its full dynamic range of intensity. Make sure that the following controls are set as indicated;

- Power Switch -> On.

- Motor -> Set to Out position.

- Scan-Stop switch -> Set to Stop.

- A %T E dial -> Set to %T.

- Time Constant -> Set to 0.1.

- Range -> Set to 0-100%. (Full clockwise)

- Sensitivity -> Set to ~1.0.

- On the sample chamber make sure both dials are set to the lead sulfide detector.

Let the spectrometer warm up for about 10 minutes and then use the following procedure to calibrate the intensity.

1) With no samples in the sample chamber, place the lid on the chamber.

2) Set the wavelength to ~1000nm using the *Wavelength* selector dial located on the left side, top of the instrument.

3) Open both the *Sample* and *Reference* shutters. The pen holder on the XY plotter should move up to hear the 100% mark.

4) Adjust the *100%* dial so that the pen holder points to the 100% mark.

5) Now close the *Sample* shutter. The pen holder should fall to near the 0% mark.

6) Adjust the *Zero* dial so that the pen holder points to 0%.

Note that since you will be recording the voltage output of the detector it is not crucial that the pen holder be set precisely to the 100% and 0% marks. The purpose of this calibration is to ensure that you are using most of the dynamic range of the detector. When properly calibrated the voltage output should be in the range 23mv to 25mv at 100% and less than 1mv at 0%.

4.2 Data Collection

There are three Si, two Ge and GaAs samples provided, each with a different thickness. For each semiconductor you can manually scan the wavelength while observing the action of the plotter pen holder to determine the approximate location of the absorption edge.

For each sample, once you have determined the approximate location of the absorption edge make careful measurements of the transmission vs. wavelength through the region where the sample goes from opaque to fully transparent.

Note that the mechanical linkage between the wavelength control knob and the optical elements can have hysteresis or slop. Calibrate this effect by comparing the absorption curve obtained by increasing the wavelength with that obtained upon decreasing it.

Make some repeated measurements under different conditions that should give the same value so as to sample your experimental uncertainty at different wavelengths. These are the uncertainties you need for the chi-squared analysis requested below.

4.3 Sample handling and properties

The samples are thin films of semiconductor mounted on cardboard sample holders. The films are polished to reduce excess reflection. They are thin and delicate. **Don't touch these films**. The GaAs sample is so thin that a free-standing film is not possible. Accordingly, it is mounted on a thicker film of another semiconductor, gallium phosphide (GaP). The light thus passes through both materials. The GaP has a wide band gap and creates negligible absorption at the light frequencies of interest. However, it does create reflection, thus complicating the multiple reflection analysis below. The index of refraction of GaP is very similar to that of GaAs, so it is OK to neglect reflections at the GaAs-GaP interface. Still, one must consider how the GaP layer modifies the reasoning of eqs.(7)-(9).

Note that the sample films are not in the center of their holders. They are positioned so that the light beam will pass through the film when the holder is oriented properly in the sample chamber. Place the sample against the lower left corner of the sample chamber against the exit opening of the spectrophotometer, with the sample labeling visible towards you.

In order to obtain percent transmission from the voltage output of the detector you need to accurately know what the voltage output is for the conditions of 100% and 0% transmission. In principle the response of the detector could vary as a function of wavelength. Although the automatic slit control feature of the Beckman spectrophotometer is designed to maintain a uniform detector response it is a point of proper experimental technique that you should quantify the detector response yourself whenever it is possible to do so. You should make measurements of the 100% and 0% voltages across the wavelength ranges corresponding to your absorption edge data. Use this data to demonstrate that the detector has uniform response or, in the case that the response is not uniform to correct your data for any non-uniformity.

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5. Data analysis

We need to extract the absorption coefficients from measurements of the fractional transmission of light through the samples. This analysis is complicated by the fact that not all of the observed light loss is due to absorption in the semiconductor. There is also loss of light due to surface reflections as the light enters and leaves the semiconductor.

When light is incident on the boundary between two materials with different indices of refraction some fraction of the light is reflected and the remainder is transmitted. For the case of normal incidence when one of the materials is air ($n \cong 1$) the fraction of light reflected (R) is given by

$$R = \left[\frac{n-1}{n+1} \right]^2 \qquad (6)$$

where n is the index of refraction of the semiconductor.

Let us now add up the light losses due to the effects of reflection and absorption as a beam of light passes through the semiconductor as shown in Figure 3.
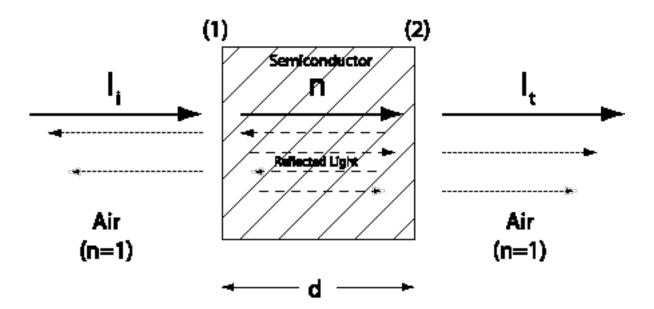

Figure 3. Passage of light through a semiconductor sample.

When the incident beam I_i enters the semiconductor at interface (1) a fraction R of the light is reflected . The remaining light I_i $(1-R)$ passes through the semiconductor suffering more loss due to absorption so that the intensity of the light at interface (2) is I_i $(1-R)e^{-\alpha d}$. At interface (2) some of the remaining light is reflected and the rest leaves the semiconductor. The light that was reflected at interface (2) propagates back to interface (1), with consequent loss due to absorption, where it is again reflected back to interface (2)... Adding up all the losses due to multiple reflections and absorption leads to an infinite series for the fraction of light transmitted through the semiconductor,

$$T = (1-R)^2 e^{-\alpha d} + R^2 (1-R)^2 e^{-3\alpha d} - \ldots$$

$$T = (1-R)^2 e^{-\alpha d} \sum_{n=0}^{\infty} (R^2 e^{-2\alpha d})^n = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \tag{7}$$

where we have normalized the incident intensity to unity $(I_i=1)$. Since $R^2 e^{-\alpha d}<1$ we can evaluate the sum and express the transmission as the ratio of the transmitted intensity I_t to the incident intensity I_i,

$$T = \frac{I_t}{I_i} = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \tag{8}$$

You can obtain the reflection coefficient R from the transmittance at photon energies $hf << E_g$ where the semiconductor is transparent and therefore $\alpha = 0$. In this case qq.(8) reduces to:

$$T = \frac{(1-R)^2}{1-R^2} \tag{9}$$

Using this R calculate $\alpha(hf)$ from eq.(8) and your measured transmittance T along the absorption edge.

Note:

$$hv = \frac{hc}{\lambda} = \frac{1241(eV)}{\lambda(nm)} \tag{10}$$

For direct band gap semiconductors E_g can be obtained by plotting α^2 against hf, from eq.(2). For indirect band gap semiconductors the quantities $E_g + E_p$ and $E_g - E_p$ can be obtained from a plot of $\alpha^{1/2}$ vs. hf. Extract the band gap energies for the different semiconductors from your data. A straight line through the upper α points of these plots intersects the x-axis at $hf = E_g$. You will find some lower α points lying above this straight line. This additional absorption is caused in GaAs by optical transitions between impurity-induced band tails (see Figs. 3 - 10 of Pankove) and in Si and Ge by phonon-assisted absorption processes.

Determine the chi-square of the fit of your data to the expected formula. Find the optimum range of energies to fit the formula. Examine the residuals to the fit and estimate the importance of effects not included in the formula. Discuss the possible causes of these discrepancies.

Using the reflection coefficients and eq.(6) calculate the index of refraction for each semiconductor and compare with the literature values. You will normally find a refractive index n somewhat larger than the literature value. This is caused (i) by imperfectly polished surfaces, which scatter light and thus reduce T in the $\alpha = 0$ region, yielding an erroneously large R value, and (ii) by the fact that n increases somewhat as hf approaches E_g. The literature value of n is measured at smaller hf.