College of Natural and Computational Sciences

Department of Physics

A Senior Project Submitted toWolkite University Department of Physics in Partial Fulfillment of the Requirement for the Degree of Bachelor of Science in Physics

Title: Temperature Dependence of Energy Band Gap of Silicon Semiconductor

By

Rahel Bekele

Advisor:

Getu Endale(M.Sc.)

Wolkite, Ethiopia

June, 2019

Acknowledgement

First of all, I would like to thank GOD! allowing me to be in these stages and able to thank all my friends that contributes to this work. I pay a very big tribute to my adviser Mr. Getu Endale for him limitless effort in guiding supervising and making critical reading of my project. He penetrating questions helped me to deepen my knowledge effectively. From him friendly approach and fatherhood advice I have learned a lot not only in the mathematics part but also to be kind, respectful and to have congregate full once again to him for all things he has done for me. I would like thank to my families and my best teacher Mr. Getu Endale for his support throughout gave me the source of power input with the reference. Finally, I would like to thank the department of physics, for all support that I have got during my study.

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List of Symbols and Abbreviations

CBM	Conduction Band Minimum
VBM	Valance Band Maximum
$g_c(E)$	The density of quantum states in conduction band
$g_V(E)$	The density of quantum states in valence
$E_g^{(0)}$	Band gap energy at absolute zero on the Kelvin
$E_g^{(T)}$	Band gap energy at any temperature
m_0	Rest mass of the electron (kg)
m_n^*, m_p^*	Electron and hole Effective mass (kg)
T	Temperature(K)
E	Charge of electron ($1.6x10^{-19}$ C)
h	Planck's constant ($1{,}054x10^{-34} Js$)
K_B	Boltzmann constant ($1.38x10^{-23} Jk^{-1}$)
$\mathbf{E_g}$	Energy band gap (eV)
N_c, N_v	Electron and hole density of accessible state (cm^{-3})
E_i	Intrinsic Fermi energy (eV)
c	Speed of light vacuum ($^m/_s$)
E_F	Fermi energy (eV)
E_a, E_d	Energy of acceptor and donor (eV)
E_c, E_V	Energy of conduction band and valance band(eV)
n_0, p_0	Thermal equilibrium concentration of electron and hole (cm^{-3})

Abstract

The energy band gap is a major factor in determining the electrical conductivity of a solid. Energy band gap is a gap of energy in solids where no electron states can exist. The energy band gap of semiconductors tends to decrease as the temperature is increased. The temperature dependence of the intrinsic carrier density is dominated by the exponential dependence on the energy band gap. In addition, one has to consider the temperature dependence of the effective densities of states and that of the energy band gap.The effective densities of holes in the valence band and the effective densities of electrons in the conduction bands are decreases with increasing energy band gap. At very low temperature, 0K both carriers remain in their respective bands and as the temperature increases carries starts to move from their bands.

Chapter 1

Introduction

1.1 Background

The beginning of semiconductor research is marked by Faraday's 1833 report on negative temperature coefficient of resistance of Silver sulfide .this is the first observation of any semiconductor property. In his 1833 paper, "Experimental Researches in Electricity" Faraday disclosed this observation. This observation was in distinction from the usual properties of metals and electrolytes in whose case resistance increases with temperature [1].

The next significant contributor to semiconductor field is the French experimental physicist Edmond Becquerel. In 1839, he reported the observation of photovoltage in the silver chloride coated Platinum electrodes. In his experiment, a AgCl coated Platinum electrode was immersed in an aqueous Nitric acid electrolyte solution. Illumination of the electrode generated photo-voltage that altered the electromagnetic field produced by the cell; in fact, it produced a reductive (cathode) photocurrent at the AgCl coated electrode. This was the first reported photovoltaic device. Photovoltage Was generated at the Ag/AgCl metal semiconductor contact, Ag at the junction was formed by the absorbed silver clusters in the AgCl electronic states [2].

The next important decade in the semiconductor research is the decade of 1870. During this period Selenium was discovered as a semiconductor, rectification at semiconductor interface came into scientists' notice. In 1873, Willoughby Smith arrived at the discovery of photoconductivity ofSelenium. He was initially working withsubmarine cables. He set into experiments with Selenium for its high resistance, which appeared suitable for his submarine telegraphy. Various experimenters measured the resistance of Selenium bars, but the resistance as measured by them under different conditions did not agree at all. Then Smith discovered that the resistance actually depends on the intensity of incident light. When the Selenium bars were put inside a box with the sliding cover closed, the resistance was the highest. When glasses of various colours were placed in the way of light, the resistance varied according to the amount of light passing through the glass. But, when the cover was removed,

the conductivity increased. He also found that the effect was not due to temperature variation [3].

For different semiconductor devices, one needs materials with different parameters, like energy band-gap. Physical properties are very different among different semiconductors due to distinct characteristics of energy band-gaps and impurities. These impurities play a major role in determining the electrical and optical properties of semiconductors. Almost all of today's technology involves the use of semiconductors, with the most significant aspect being the integrated circuit (IC).

1.2 Statement of problem

Our researchers were shown that the concept of temperature dependence of energy band gap of silicon semiconductor. We will be conducted the study in order to create a good understanding of the topic to anyone who are interested on this title and to present the topic in understandable and simple manner. This research project work will be expected to answer the following question at the end of research work.

- Are the temperature effects of on energy band gap of silicon?
- What is the Effects of Energy band gap on carrier's concentration and effective densities of carrier concentration of silicon?

1.3Objectives of the study

1.3.1 General objective

The general objective of the study is to study understand the temperature dependence of energy band gap of silicon semiconductor.

1.3.2 Specific objectives

The specific objectives of this study are:-

- To know the temperature effects of on energy band gap of silicon
- To explain effects of Energy band gap on carrier's concentration and effective densities of carrier concentration of silicon

1.4 Significance of the Study

This project studieshas been focused on temperature dependence of energy band gap of silicon semiconductor. The aim of this work is to develop a better understanding how temperature depends on energy band gap for silicon semiconductor. It serves as reference for researcher doing on the same topic in the future. Another significance of this paper is for students who take this course to get information for their preparation for exam and develop their knowledge.

1.5 Scope of the Study

My studies have been focus on the collection of energy levels associated with the outer shell electrons (valence electrons) is called valence band. This is of outmost importance is determining the electrical and optical properties of the material. The valence band might be completely filled or half filled.It can never be empty.

Now, if the electrons in the valence band gain sufficient energy they can become free electrons .They will be free to move about the entire material.The collection of energy levels associated with the free electrons (since the free electrons are responsible for conduction they are called conduction electrons) is called conduction band. The extra energy required by a valence electron to move to the conduction band is called the forbidden energy. Depending on the magnitude of free energy we can characterize materials as metals, insulators and semiconductor.

1.6 Limitation of the project

On the process of carrying out some activity challenges was happened. There are somelimitations while doing this project work:

- There is no enough book,
- Lack of internet accessibility,
- Lack of more time to do this project,
- Lack of budget.

Mostly the Lack of internet accessibility was enforced me to narrow the project and it would make me to do the project narrowly.

1.7 Outline

In this work the effects of temperature on energy band gap of silicon semiconductor is studied.The study is organized into five chapters. InChapter onethe background, statement of problem, objectives of the study and significance of the study of the temperature dependence of energy band gap of silicon semiconductor were discussed.Chapter two is literature review.In literature review, Energy band gap in semiconductors; Intrinsic and Extrinsic semiconductors were also deeply explained.Chapter three describes the overall methodology by which important data is collected and analyzed. Chapter four covers the results and discussion of the study. Chapter five gives the conclusion and outlook of the study.

Chapter 2

Literature Reviews

2.1. Energy band gap in semiconductors

The energy band gap is a major factor in determining the electrical conductivity of a solid. Energy band gap is a gap of energy in solids where no electron states can exist. Energy band gap, also called an energy gap or band gap. The band gap generally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. The closest point between the top of the valance band curve and the bottom of the conduction band is called the materials Energy Gap. For insulating materials, this gap can be greater than ten electron volts. However, for semiconductor electronic devices operating a reasonable voltage, the gap has to be a few electron volts [4].

The band gap of a semiconductor, given by the energetic difference between its valence band maximum and conduction band minimum, has important implications for both the semiconductor's light absorption properties and the maximum photo voltage that can be expected from a corresponding device. In order to absorb a photon, an electron generally must be excited from the valence band of the semiconductor to the conduction band. Thus, a photon must possess energy greater than or equal to that of the semiconductor band gap in order to be absorbed and create an excited electron-hole pairs. The processes excitation of free carriers must obey the law of energy and momentum conservations. This, in particular, leads to the fact that the minimum quantum energy sufficient to excite electron from the valence band to the conduction band is equal to the band gap of the semiconductor. The energy bands may be occupied or unoccupied. The highest occupied band is called the valence band at energy E_V, and contains the valence electrons. The lowest unoccupied band is called the conducting band that lies at the energy level E_C. The energy bands can be empty, partly full or completely full and determines the properties of the solid. The band gap energy E_g is the energy deference between the valence and the conduction band [5].

$$E_g = E_C - E_V. \quad (1)$$

The thermal excitation of electrons from the valence band to the conduction band creates free carriers in both bands. A large band gap will make it more difficult for a carrier to be thermally excited; hence the concentration of thermal carriers is lower in higher band gap materials [6].

The first empirical relation for the band gap shift with temperature developed by varshini*etal*was given by [7]:

$$E_g(T) = E_{g0} - \frac{\alpha T^2}{\beta + T}, \tag{2}$$

Where$\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are constants choosen to obtain the best fit to experimental data and $\boldsymbol{E_{g0}}$ is the limiting value of the band gap at zero Kelvin. It was found that $\boldsymbol{E_{g0}}$= 1.166eV, α = 4.73 x 10^{-4}eV/K and$\boldsymbol{\beta}$ = 636 K for silicon[8].

2.2. Intrinsic and Extrinsic semiconductors

The semiconductors may be divided into two categories; the pure un doped semiconductor, which is usually referred to as the intrinsic semiconductor, and the doped semiconductor, which is also called the extrinsic semiconductor. The total thermal equilibrium density of electrons in a semiconductor is given by [9]:

$$n_0 = N_C \exp\left(-\frac{E_C - E_F}{k_B T}\right), \tag{3}$$

Where,

$$N_c = 2\left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{3/2} \tag{4}$$

is the effective density of the conduction band states, m_n^* is effective mass of electrons in the conduction band and h is the known Planck's constant. The hole thermal equilibrium density in the valence band is also given by:

$$p_0 = N_V \exp\left(-\frac{E_F - E_V}{k_B T}\right), \tag{5}$$

Where,

$$N_V = 2\left(\frac{2\pi m_p^* k_B T}{h^2}\right)^{3/2} \tag{6}$$

andm_p^* is effective mass of holes in the valence band. The values of m_p^* and m_n^* for silicon (si) is given by [10]:

$$m_p^* = 0.56m_n \text{and} \quad m_n^* = 1.1\, m_n, \tag{7}$$

Where, m_n is the rest mass of electron which is equal to9.11×10^{-31}kg.

2.2.1. Intrinsic semiconductors

Semiconductors are considered to be as intrinsic semiconductors if it's thermally generated carrier density represented by n_i is much larger than the background doping or residual impurity densities. At room temperature ($T = 0K$), an intrinsic semiconductor behaves like an insulator because the conduction band states are totally empty and the valence band states are completely filled. However, as the temperature increases, some of the electrons in the valence band states are excited into the conduction band states by thermal energy, leaving behind an equal number of holes in the valence band. Suppose that $\mathfrak{N}$ is the concentration of electron-hole pairs thermally generated in the respective bands and $\mathfrak{N}_R$is the concentration of electron hole annihilated after the generation, the free carrier concentrations in the conduction and valence bands adjust for the intrinsic semiconductor to be:

$$n_0 = \mathfrak{N} - \mathfrak{N}_R = n_i = p_0. \tag{8}$$

Since the non-degenerate relations are obviously valid for an intrinsic semiconductor, the intrinsic carrier concentrations are given as follows:

$$n_i = N_C \exp\left(-\frac{E_C - E_i}{k_B T}\right) = N_V \exp\left(-\frac{E_i - E_v}{k_B T}\right), \tag{9}$$

where, E_F is the Fermi level, $E_i$intrinsic energy level and k_BBoltzmann constant which is equal to$1.38 \times 10^{-23}\text{JK}^{-1}$.

The intrinsic Fermi energy derived from effective density of electron andholes as follows:

$$E_i = \frac{E_C - E_V}{2} + \frac{k_B T}{2} \ln\left(\frac{N_V}{N_C}\right). \tag{10}$$

or

$$E_i = \frac{E_V + E_C}{2} + \frac{3}{4} k_B T \ln\left(\frac{m_p^*}{m_n^*}\right), \tag{11}$$

Which indicates that if $m_p^* = m_n^*$ or $T = 0$ the Fermi level in an intrinsicsemiconductor is positioned at mid-gap. In real cases $m_p^* \neq m_n^*$,resulting in small deviation of the Fermi level from mid-gap.

The equilibrium density of electrons and holes in a non-degenerate semiconductor is constant at a given temperature. The product of the electrons and holes density, in a non-degenerate semiconductor at equilibrium, is always equal to the square of the intrinsic carrier density [11]:

$$n_i{}^2 = p_0 n_0 \tag{12}$$

The intrinsic carrier density (which is specific to a given semiconductor) is related to the effective density of conduction and valence band, i.e.

$$n_i = \sqrt{N_C N_V} \exp\left(\frac{E_V - E_C}{2k_B T}\right). \tag{13}$$

This relationship, referred to as the law of mass action, which allows (at thermal equilibrium) to determine the electron density if the hole density is known or vice versa. It should be noted that this equation signifies that, the electron-hole pairs may be continuously generated and recombined; the product of the concentration (averaged in time) stays constant. This equation also indicates that, for a non-degenerate material in equilibrium, the $p_0 n_0$ product depends on the effective conduction and valence band densities of states, the energy band gap of a semiconductor, and the temperature. It is independent of the Fermi level position and of the individual electrons and holes densities. In other words, the $p_0 n_0$ product is constant at a given temperature regardless of doping.

2.2.2. Extrinsic Semiconductors

The availability of charge carrier's in the valence and conduction bands greatly affected by the presence of impurities (*i.e.*, foreign atoms incorporated into the crystal structure of a semiconductor). In semiconductors, some impurities are deliberately introduced to produce materials and devices with desired properties. The process of putting impurities into the lattice is doping. The contribution of free carriers by dopants requires them being ionized (i.e., the dopants have donated or accepted an electron). The ionization of the dopants depends on the thermal energy and the position of the impurity level in the energy gap of a semiconductor. In an extrinsic semiconductor, electrons are majority carriers and holes are

minority carriers in n-type semiconductor. In p-type material, electrons are minority carriers and holes are majority carriers [12].

As shown in the Figure 1 below, at low temperature, the donor impurity levels are filled. But with increasing T, the electron in the donor levels are excited into the conduction band and similarly the holes in the acceptor levels are excited into the valence band. With a small temperature, these donors or acceptors can be thermally excited into the band. Therefore, the donor impurities donate free electrons to the conduction band, whereas the acceptor impurities give free holes to the valence band. However, at very low temperature, these carriers are bound back to their respective nuclei so that they can no longer carry electricity, a phenomenon known as carrier freeze out [13].

Figure 1 also shows that, when donor impurities are added, at zero temperature, these states are near the top of the band gap, and are filled. Thus, the Fermi energy is moved up to the top of the band gap. On the other hand, when acceptors are added, the acceptor states near the bottom of the band gap are empty. (Remember it is a bound state of a hole to a nucleus!). Thus, the Fermi energy is moved down to the bottom of the band gap. The presence of impurities in a material can have dramatic effects on its optical properties. There are two main optical effects of impurities. The first effect is that the impurities add charge carriers to the materials. This obviously can have some important effects on the interaction with light. The second important effect is the introduction of new energy levels within the gap. Whereas before the introduction of impurities, the lowest energy transition that can be made is the full energy of the gap, now one can have optical transitions between impurity states, or from the bands to the impurity states [14].

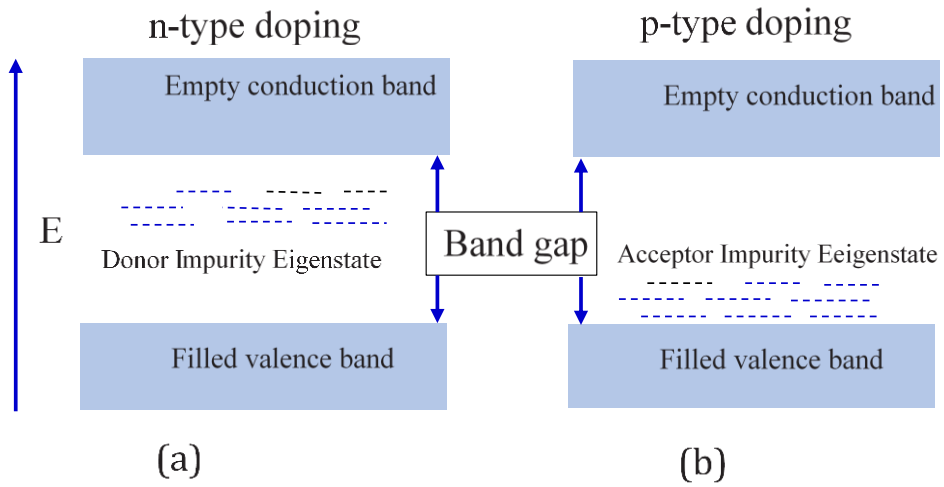

Figure 1: Doped semiconductors with (a) donor (b) acceptor impurities.

The most important and unique feature of a semiconductor material lies in the fact that its electrical conductivity can be readily changed by many orders of magnitude by simply doping the semiconductor with shallow-donor or shallow-acceptor impurities. By incorporating the doping impurities into a semiconductor, the electrons or holes density will increase with increasing shallow-donor or shallow-acceptor impurity concentrations. Adding donor or acceptor impurity atoms into semiconductor will change the distribution of electrons and holes in the material, and as a result, the Fermi energy will change.

$$n_0 = n_i \exp\left(-\frac{E_i - E_F}{k_B T}\right) \text{and} p_0 = n_i \exp\left(-\frac{E_F - E_i}{k_B T}\right). \quad (14)$$

Chapter 3

Methodology

The first step in this work is to select an appropriate semiconductor sample in which the temperature dependence of energy band gap of semiconductor is studied, that is silicon semiconductor. The next step is to collect important data for the parameters of the semiconductor used in the description of its electrical and optical properties. Next by using the existing data of the majority carrier concentration for the selected sample, the simulation for the energy band gap as function of temperature is described.To write this senior project, we used previous written source and gather extra information from internet this project working of the study by reviewing article temperature dependence of energy band gap of silicon semiconductor. Based on the published article, the necessary information for the research work has been gathered.The information for this study will gathered in difference ways. The source of information is only secondary source of data. The sources information is published article, internet, and text books.

Chapter 4

Results and Discussions

4.1. Effects of Temperature on Energy band gap of silicon

The temperature dependence of the energy band gap has been expressed by using equation (2). For E_g as a function of the temperature T, a plot of the resulting band gap versus temperature is shown in the figure below for silicon semiconductor.

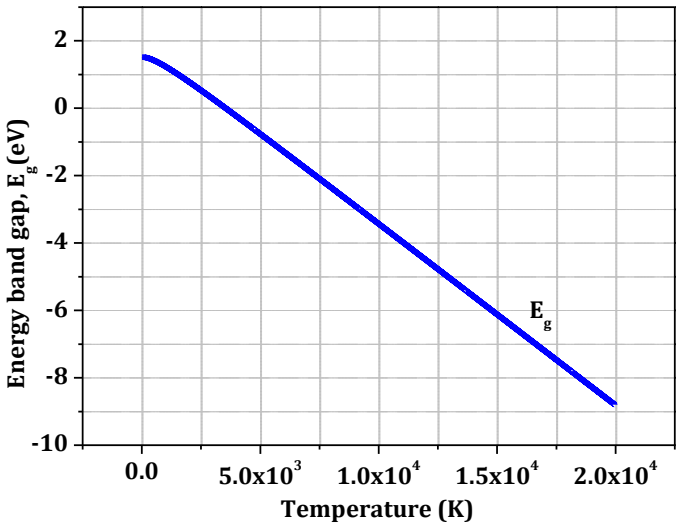

Figure 2: Temperature dependence of the energy band gap of silicon (blue curve), which shows how the band gaps of the silicon decreases as temperature increases (the labeled points are the band gap of each material at room temperature).

As we can see from the above figure, the energy band gap of semiconductors tends to decrease as the temperature is increased.As temperature increases, the band gap energy decreases because the crystal lattice expands and the interatomic bonds are weakened. Weaker bonds means less energy is needed to break a bond and get an electron in the conduction band.

4.2. Effects of Energy band gap on carriers concentration of silicon

For an electron-hole pair to be created in an intrinsic semiconductor, a bond must be broken in the lattice, and this requires energy. An electron in the valence band must gain enough energy to jump to the conduction band and leave a hole behind. As the energy band gap is increased, the number of broken bonds (carriers) decreases because there is more thermal energy available so more and more electrons gain enough energy to break free. As the energy band gap is increased, electrons do not receive enough energy to break a bond and remain in the valence band. If electrons are in the conduction band they will quickly lose energy and fall back to the valence band, annihilating a hole. Therefore, lowering the energy band gap causes a increase in the intrinsic carrier concentration, while raising the energy band gap causes an decrease in intrinsic carrier concentration.A plot of the resulting band gap versus carrier's concentration is shown in the figure below for silicon.

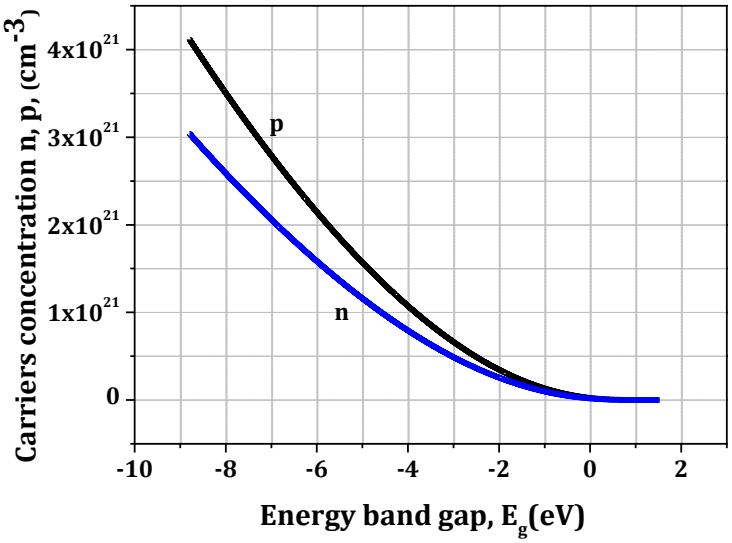

Figure 3: Energy band gap dependence of the carrier's concentration of silicon, which shows how the band gaps of the silicon as temperature increases (the labeled points are the band gap of each material at room temperature).

4.3. Effects of Energy band gap on effective densities of carrier concentration of silicon

A plot of the effective densities of carrier density versus temperature is shown in figure 4 below for silicon.This plot is based on the relations given in equation (4) and (6) above for effective densities of holes in the valence band and effective densities of electrons in the conduction band respectively.

As we can see fromfigure below, both the effective densities of holes in the valence band and the effective densities of electrons in the conduction bands are decreases with increasing energy band gap. At very low temperature, 0K both carriers remain in their respective bands and as the temperature increases carries starts to move from their bands. This means that if the energy band gap is large, the probabilities of carriers to move from their band to other is small and if the energy band gap is small, the probabilities of carriers to move from their band to other is large. So, for large energy band gaps, the electrons from thevalence band can't jump to conduction band and their probabilities to remain in the valence band increases.

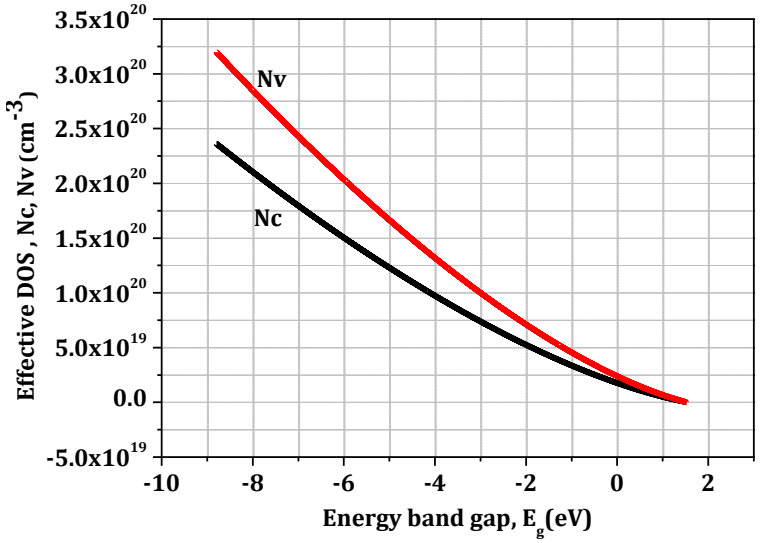

Figure 4: Effective densities of states versus energy band gap in silicon.

4.4. Effects of temperature on the position of energy bands

The figure 5 below shows the effects of temperature on the conduction band, valence band and intrinsic energies for the silicon elemental semiconductor.

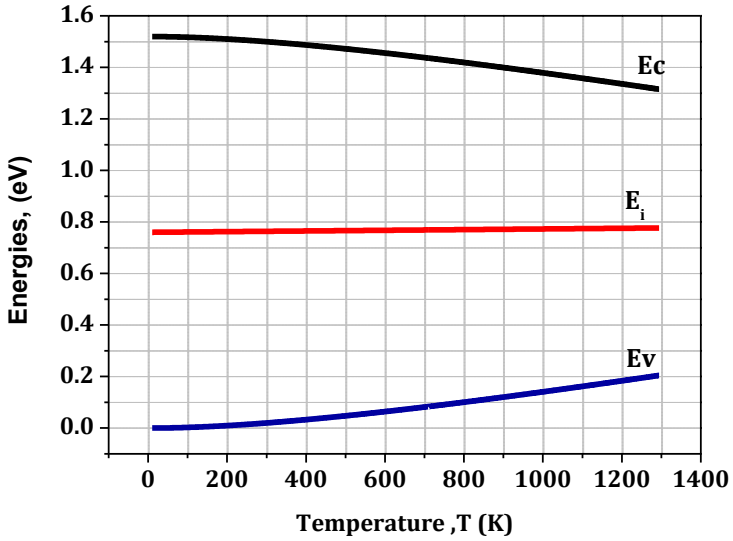

Figure 5: Effects of temperature on the position of energy bands

The result revealed that, at 0K or low temperature, the energy of conduction band and energy of valence band was on the same position. But as temperature increases, from 200K to 1200Kthe valence and conduction band energies bends to intrinsic energy.

Chapter 5

Conclusion and Outlook

5.1. Conclusion

Generally, the energy band gap of semiconductors tends to decrease as the temperature is increased. The temperature dependence of the intrinsic carrier density is dominated by the exponential dependence on the energy band gap.Based on mobility's, Si would be the material to choose for higher conductivity but Si also has a higher band gap so that the intrinsic carrier concentration would be low. A higher mobility can lead to an increase in conductivity the dominant term is the carrier concentration and consequently the band gap.

Under low temperatures, the effect of lattice expansion on the band gap energy is very small, but it has much influence on the band gap energy at high temperatures. Therefore, it is necessary to consider the effect of lattice expansion at high temperatures, and the method considering the effect of lattice expansion has also been given.The band gap energy, of silicon and its temperature dependence in the temperature range of 200 K to 1200 K was investigated. The data is in good agreement with the earlier known values in the literature.

5.2. Outlook

In general, the study will further investigate the role of temperature dependence of conductivity in (Si) semiconductors. This particularly study gives more about the band gap of semiconductor and explain especially the silicon materials. The study will further investigate the role of temperatureon energy band gap of silicon semiconductors. The future work is to determine the remaining parametersthat are completely describes electrical and optical properties of silicon semiconductors and focusing on their application.

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