Effects of Shallow Versus Deep Acceptors on the Photo Response of P-type Gallium Antimonide(Gasb) Semiconductor

By

Haregua Bogale

A Thesis Submitted to

The department of Applied Physics

School of Applied Natural Science

Presented in Partial fulfillment of the requirements for the degree of Master's in Physics

Office of Graduate Studies

Adama science and Technology University

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Declaration

I hereby that this MSc Thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis has been duly acknowledged.

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Signature……..

This MSc Thesis has been submitted for examination with my approval as thesis advisor.

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Signature……..

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Abstract

In this study the effects of shallow versus deep acceptors on the photo response of p-type Gallium antimonide (GaSb) semiconductors from the simulation of the temperature dependence of the majority carrier concentrations measured using Hall Effect measurements. By fitting the measured values of the temperature dependence of the majority carrier concentrations with the theoretical description of the data obtained from the theoretical simulation of the ionization of the deep and shallow acceptors, the energies corresponding to each acceptor can be determined for different doping level samples. The contribution of shallow level acceptors to the thermal equilibrium carrier density is very high as compared to the deep level acceptors of the same impurity concentration. This can be extended to the determination of radiative excess carrier lifetime for the description of the photo-response of the material versus shallow and deep acceptors.

Chapter one

Introduction

1.1 Background of the study

According to G. Busch, the term "semiconducting" was used for the first time by Alessandro Volta in 1782[1]. The first documented observation of a semiconductor effect is that of Michael Faraday (1833), who noticed that the resistance of silver sulfide decreased with temperature, which was different from the dependence observed in metals [2]. Semiconductors can be divided into two categories:

1. The pure or un-doped semiconductor that is usually referred to as intrinsic semiconductor;
2. The doped semiconductor that is called an extrinsic semiconductor.

The difference between a metal and a semiconductor is that the electrical conduction in a metal is due to electrons, while the electrical conduction of a semiconductor may be attributed to electrons, holes, or both carriers. The electrical conduction of an intrinsic semiconductor is due to both electrons and holes, while for an extrinsic semiconductor electrons or hole, depending on whether the semiconductor is doped with shallow donors or shallow acceptors, usually dominates it [3].

A shallow donor refers to a donor that contributes an electron that exhibits Energy states equivalent to atomic hydrogen with an altered expected mass that the long-range coulomb potential of the ion cores determines the energy level [4]. Essentially, the electron orbits the donor ion within the semiconductor material approximately the Bohr radius. This is in contrast to the deep level donors where the short-range potential determines the energy levels not the effective mass states. This contributes additional energy states that can be used for conduction band. Introducing impurities in a semiconductor, which are used to set free additional electrons in its conduction band, is called doping with donors. In a group IV semiconductor like Silicon, the most often group five elements like Arsenic or Antimony can be added as donors [5] .

However, these impurities introduce new energy levels in the band gap affecting the band structure which may alter the electronic properties of a semiconductor to a great extent. Having shallow donor level means that these additional energy levels are not more than $3k_BT$ (0.075 eV) at room temperature away from the lower conduction band edge. This allows as treating the original semiconductor as unaffected in its electronic properties, with the impurity atoms only increasing the electron concentration. A limit to donor concentration in order to allow treatment as shallow donors is approximately (10^{19} cm^{-3}). Energy levels due to impurities deeper in the band gap are called deep levels [7].

A semiconductor is a crystalline material which, at absolute zero temperature, is a perfect insulator due to the inability of electrons to move and conduct charge. Yet, at increased temperatures, the semiconductor is able to conduct due to the presence of thermally excited electrons. The phenomenon of semiconductors is understood by the theory of allowed and forbidden energy bands, which is based on the quantum mechanical representation of solids. The theory of solids infers the overlap of the electronic wave functions of the atoms and the subsequent formation of discrete energy bands for the electrons [8]. The nature of the discreteness permits the electron to exist in some regions of energy and momentum, while in other regions the electron is forbidden. Electrons (fermions) will occupy the available bands starting at the lowest energy level and successively fill higher levels. Because it is the electrons which conduct current, those electrons in filled bands have no higher energy levels available to them and therefore do not conduct. If the energy gap between the top most filled band and upper empty band is large, then the material is an insulator. On the other hand, if the electrons do not fill up the band and the material has many energy levels available for the electron to occupy, the material is a conductor. If the upper most filled band is separated from a higher but empty band by small energy spacing, the material is classified as a semiconductor. A change in the crystal structure from the perfect lattice is called a defect. Defects occur by a number of different means but one major defect is that of an impurity. The most modern production techniques still allow the development of impurities. The final result of such impurities is that energy levels develop within the band gap. The presence of energy levels within the band gap of the

material indicates the impurity has resulted in the formation of electron or hole states with in what is normally a forbidden zone [9].

Substitutional impurities can create additional energy levels known as donor or acceptor levels. The substitutional atom, while bonding with native atoms, may alter the coulomb electrostatic forces and shift the energy distribution [9] . A donor energy level is located slightly below the bottom of the conduction band while acceptor levels are above the valence band. The donor occurs when the impurity has a valence greater than the atom it replaced, since the greater valence means it has electrons not needed for bonding; these electrons may be donated to other processes. GaSb is a semiconductor formed of periodic table Group III-V elements Ga and Sb. It belongs to antimonide compound semiconductors family which has a smaller band gap among III-V semiconductors, making them suitable for optoelectronic devices operated in the infrared region and electronic devices in the wave length range 1-5 μm and has an energy band gap of 0.727 eV (1.71 μm) at room temperature and 0.813 eV (1.527 μm) at 4K. An element from Group VI, such as tellurium, is the impurity; it has an extra electron which is only loosely bound to the tellurium atom in the lattice. When the substitutional impurity is due to a Group II element, such as zinc, an acceptor level is formed due to the shortage of electrons. The shortage is filled in the process of creating a hole. The binding energy of the hole or electron to an impurity is similar to the exciton energy equation, however the interpretation of m* is now the effective mass of the electron or hole. The electron or hole can be removed from the impurity if it is excited to the conduction or valence band; the impurity is now ionized with the loss of the charged particle. Other defects in the crystal can also have significant effects on the semiconductor properties. The strain introduced by a lattice mismatch, for example a GaSb layer on a GaAs substrate, can alter the energy levels. A vacancy at a lattice point effectively creates an impurity, which can form either an acceptor or an acceptor complex; because the bonding needs are no longer being satisfied.Gang Chen *et al*. Studies about the effect of shallow versus deep level doping on the performance of thermos-electric material to maximize the device efficiency [10]. This work also concerns about the effect of shallow versus deep acceptors for the efficient use of thermoelectric materials in optoelectronic devices.

1.2 Objectives of the Study

1.2.1. General Objectives

The general objective of this study is to determine the effects of shallow versus deep acceptors on the photo response of Gallium antimonde semiconductors.

1.2.2. Specific objectives of the study

- to describe the contribution of shallow acceptors on the entire thermal equilibrium majority carrier concentration of GaSb ,
- to describe the contribution of deep acceptors on the entire thermal equilibrium majority carrier concentration of GaSb ,
- to determine the effects of deep versus shallow acceptors on the photo-response of GaSb.

Chapter two

Litrature review

Under this topic the thermal equilibrium properties and the photo-responses of a p-type semiconductors especially that of the properties related to Gallium antimonide (GaSb) is discussed in detail.

2.1 Thermal properties of semiconductors

2.1.1 Energy band theory

Energy band gap is an energy range in a solid where no electron states can exist due to the quantization of energy in quantum mechanics [11]. Electrical conductivity of non-metals is determined by the susceptibility of electrons to excitation from valance band to conduction band. In solid state physics, the valance band and conduction band are the bands closest to the Fermi-level and thus determine the electrical conductivity of the solid. The valance band is the highest ranges of electron energies in which electrons are normally present at absolute zero temperature, while the conduction band is the lowest range of vacant electronic states. On a graph of the electronic band structure of a material, the valance band is located below the Fermi-level, E_F, while the conduction band is located above the Fermi-level. The electrical conductivity of a solid depends on its capability to flow electrons from valence band to conduction band. The band gap energy, E_g is represented by the difference between the energy of the CBM, E_C and the VBM, E_V:

$$E_g = E_C - E_V. \tag{1}$$

Hence in case of a semi metal with an over-lap region, the electrical conductivity is high. If there is small band gap energy, then the flow of electron from valence to conduction band is only possible if an external energy (thermal, optical *etc.*) is supplied and these groups with small E_g are called semiconductors.

When the conduction band minima (CBM) and the valence band maxima (VBM) occur at the same value of electronic wave vector, *k*, the material is said to be direct-band material. Conversely, when the CBM and the VBM occur at different values of *k*, the material is said to be indirect-band material. Electronic transitions between the two bands in a direct material can take place with little or no change in crystal momentum. On the other hand, conservation of momentum during an interband transition is a major concern in indirect-band materials. GaSb is an example of a direct-band material, while Ge and Si are indirect materials. The direct or indirect nature of a semiconductor has a very significant effect on the properties exhibited by the material, particularly the optical properties. The direct nature of GaSb, for example, makes it ideally suited for use in semiconductor lasers and infrared light-emitting diodes and other optoelectronic devices. Band gap energy is perhaps the most important in semiconductor physics.

The energy band gap determined at thermal equilibrium condition is known as the thermal band gap of the semiconductor. On the other hand, the energy band gap of a semiconductor can also be determined using the optical absorption measurements near the absorption edge of the semiconductor. The energy band gap thus determined is usually referred to as the optical band gap of the semiconductor. A small difference between these two band gap values is expected due to the difference in the measurements of optical and thermal band gaps. Since the energy band gap for most semiconductors decreases with increasing temperature, a correction of E_g with temperature is necessary. A contraction of the crystal lattice with decreasing temperature usually leads to a strengthening of the interatomic bonds and an associated increase in the band gap energy.

The first empirical relation for the band gap shift with temperature was developed by Varshni et al. [4]:

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

Where $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are constants chosen to obtain the best fit to experimental data and $\boldsymbol{E_{g0}}$ is the limiting value of the band at zero Kelvin. For GaSb semiconductor $\boldsymbol{E_{g0}}$ is equal to 0.813 eV, $\boldsymbol{\alpha}$ is equal to $\mathbf{3.78 \times 10^{-4}\ eV/K}$ and that of $\boldsymbol{\beta}$ is equal to 94 K.

2.1.2 Thermal equilibrium carrier concentration

Unlike metals, the electrical conductivity of a semiconductor can be changed by many orders of magnitude by simply adding impurities or by using external excitations (e.g., by thermal-excitation). At low temperatures, a pure semiconductor may become a perfect electrical insulator, since its valence band is totally filled with valence electrons and the conduction band is completely empty. However, as the temperature rises, a fraction of the valence electrons are excited into the conduction band by the thermal energy, thus creating free holes in the valence band. As a result, the electrical conductivity will increase rapidly with increasing temperature [13]. Therefore, a semiconductor may become a good electrical conductor at high temperature.

A unique feature of semiconductor materials is that the physical and transport parameters depend strongly on temperature [11]. For example, the intrinsic carrier concentration of a semiconductor depends exponentially on temperature. Other physical parameters, such as carrier mobility, resistivity, and the Fermi level in a lightly doped semiconductor, are likewise a strong function of temperature. In addition, both the shallow level and deep-level impurities may also play an important role in controlling the physical and electrical properties of a semiconductor. For example, the equilibrium carrier concentration of a semiconductor is controlled by the shallow-level impurities, and the minority carrier lifetimes are usually closely related to defects and deep-level impurities in a semiconductor. The equilibrium distribution functions for electrons in the conduction band and holes in the valence band may be described in terms of the F-D distribution function .The F-D distribution function for electrons in the conduction band is given by [13]:

$$f_n(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}, \tag{3}$$

where E is energy of the electron, E_F, the fermi-energy, k_B, Boltzmann constant and T, temperature of the material. The F-D distribution function for hole with energy E in the valence band is also expressed by:

$$f_p(E) = 1 - f_n(E) \approx 1 - \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)} \tag{4}$$

or

$$f_p(E) = \frac{1}{1 + \exp\left(\frac{E_F - E}{k_B T}\right)} \tag{5}$$

Then the total thermal equilibrium density of electrons in a semiconductor is given by:

$$n_0 = N_C \exp\left(-\frac{E_C - E_F}{k_B T}\right), \tag{6}$$

where

$$N_c = 2\left(\frac{2\pi m_n^* k_B T}{h^2}\right)^{3/2} \tag{7}$$

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:

$$p_0 = N_V \exp\left(-\frac{E_F - E_V}{k_B T}\right), \tag{8}$$

Where

$$N_V = 2\left(\frac{2\pi m_p^* k_B T}{h^2}\right)^{3/2} \tag{9}$$

and m_p^* is effective mass of holes in the valence band. In general, the semiconductors may be divided into two categories: the pure undoped semiconductor, which is usually referred to as the intrinsic semiconductor, and the doped semiconductor, which is also called the extrinsic semiconductor.

2.1.3 Intrinsic semiconductor

A semiconductor may be considered as an intrinsic semiconductor if its thermally generated carrier density represented by n_i is much larger than the background doping or residual impurity densities [14]. At T = 0 K, 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:

$$n_0 = \mathfrak{N} - \mathfrak{N}_R = n_i = p_0, \tag{10}$$

where n_0 and p_0 denote the equilibrium electron and hole densities, respectively. Since the non-degenerate relations are obviously valid for an intrinsic semiconductor where the Fermi-level, E_F is equal to the intrinsic level energy, E_i in the semiconductor, one can write the form:

$$n_i = N_C \exp\left(-\frac{E_C - E_i}{k_B T}\right) = N_V \exp\left(-\frac{E_i - E_V}{k_B T}\right). \tag{11}$$

Then, the intrinsic energy is expressible as:

$$E_i = \frac{E_V + E_C}{2} + \frac{3}{4}(K_B T)\ln\left(\frac{m_p^*}{m_n^*}\right) \tag{12}$$

The electron-hole pairs in an intrinsic semiconductor are generated by thermal excitation. Therefore, for intrinsic semiconductors with an energy band gap on the order of 1 eV or higher the intrinsic carrier density is usually very small at low temperatures below 100 K. As a result, the resistivity for these intrinsic semiconductors is expected to be very high at low temperatures. The intrinsic carrier density increases with increasing temperature.

2.1.4 Extrinsic Semiconductors

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. Incorporating the doping impurities in to a semiconductor, the electron or hole density will increase with increasing shallow-donor or shallow-acceptor impurity concentrations. One of the many types of the materials that are technologically

important to day, semiconductor crystals require the greatest level of impurity control while a metal is considered extremely pure with contaminant concentrations as high as one part in ten thousand, or $\sim 10^{18}$ atoms cm^{-3}, semiconductor devices can require crystal materials with less than 10^{15} electrically active impurities per cm^3. The control of the type and amount of impurity in the various parts of a semiconductor material is key in the construction of any device. Electronic impurities in semiconductor crystals are generally grouped in two large categories [14]: shallow and deep levels. Depending on the Size of the band gap, a level may be regarded by its energetic location as deep, but may be shallow in a wide-band gap semiconductor.

Shallow levels have a large interaction with one band, which is due to the large extension of its electron wave-functions. The electrons are loosely bound to the impurity and thus move similar to free electrons but with a different mass. The thermal energy at room temperature is enough to ionize a large amount of the levels, meaning emission of charge carriers to the adjacent bands; thus they are used as donor or acceptor levels. The potential of shallow levels can be approximated by a hydrogen-like coulomb potential screened by dielectric permeability of the host lattice and with modified effective masses. Effective mass theory calculates very well the energetic position of the excited states but deviates from the observed ground state energies. Electrons in the ground state feel more the core environment, which is different from that of a point charge. Shallow levels are used to control the Fermi-level in the semiconductor, thus they can be intentionally introduced into the semiconductor to define the donor- and acceptor concentrations, N_d and N_a, respectively, *i.e*. the available charge carriers needed for conductivity. The shallow-level density can be measured from HALL- or capacitance-voltage investigations, whereas the energetic location is determined by temperature-dependent Hall Effect measurement or photoluminescence measurements.

The other categories of semiconductor impurities are deep level defects which lie throughout the energy gap. Further, one impurity element can introduce more than one defect level in the band gap. Theoretical models for this group of defects are clearly less accessible than in the case of shallow impurities. Even in the simplest case of a simple substitutional deep impurity, the hydrogenic model is not useful because

the wave functions are too highly localized. Analysis is more complicated for interstitial defects and defect complexes. The defect can bind carriers more strongly than a shallow level, so the energy level of the defect may be located closer to the mid gap. Since the orbital of an electron of an electron or hole bound to a deep level defect is smaller than that of less tightly bound carrier orbiting a shallow impurity. The extent of the level in k-space is correspondingly greater. Thus, a single extremism is not sufficient for a theoretical description of a deep level defect. Deep levels have a short steep potential [15]. Their electron wave functions are largely localized at the defect site. The shallow donor (acceptor) levels emit their electrons (holes) to the conduction band edge, E_C or valence band edge, E_V, where they travel freely and contribute to the conductivity. The free charge carriers may be trapped by deeper levels, where they are frozen out unless enough thermal energy is provided to excite them back to the bands again.

Deeper located levels can interact with both bands easily and the free charge carriers may use these defect states as recombination path. For example, electron or hole densities can increase from 10^{13}cm^{-3} to more than 10^{20}cm^{-3} if a shallow-donor or shallow-acceptor impurity with an equal amount of impurity densities were added into a gallium crystal. An extra electron from the group-V atom is added to the host silicon lattice. Since this extra electron is loosely bound to the substitutional impurity atom (i.e., with ionization energy of a few tens of meV), it can be easily excited into the conduction band via thermal energy, and hence contributes to free electrons in the conduction band at 300 K. If the electrical conduction is due to electrons, then it is called an n-type semiconductor. A doping impurity that provides an extra electron per impurity atom to the host semiconductor is called a shallow-donor impurity. Thus, group-V elements in the periodic table are usually referred to as shallow-donor impurities for group-IV elemental semiconductors such as Si and Ge. If a group-III element is introduced into a group-IV elemental semiconductor, then there is a deficiency of one electron for each replaced host atom by a group-III impurity atom, leaving an empty state (or creation of a hole) in the valence band. In this case, the conduction process is carried out by holes in the valence bands, and the semiconductor is called a p-type semiconductor. The group-III elements including boron, gallium, and

aluminum are common doping impurities for producing p-type doping in the elemental semiconductors. Thus, group-III elements are shallow-acceptor impurities for the elemental semiconductors. In addition to the relatively shallow-level donors and acceptors, the substitution of other impurity atoms into a host semiconductor can give rise to deep-level states allowed states in the band gap more than a few tenths of an eV from either band edge. These are commonly referred to as traps or recombination-generation centers. Such centers are usually unintentional impurities, are not necessarily ionized at room temperature, and typically occur in concentrations far below the dopant concentration. The deep level centers can be donor like (positively charged when empty and neutral when filled with an electron), Acceptor like (neutral when empty and negatively charged when filled with an electron), or may exhibit multiple charge states with associated multiple levels in forbidden gap.

In semiconductors, current conduction by holes is as important as electron conduction in general. It is important to become familiar with thinking of the holes as mobile particles carrying positive charge, just as real as conduction electrons are mobile particles carrying negative charge. It takes about 1.1 eV of energy to free a covalent electron to create a conduction electron and a hole. This energy can be determined, for example, from a photoconductivity experiment [16]. When light shines on a Si sample, its conductivity increases because of the generation of mobile electrons and holes. The minimum photon energy required to induce photoconductivity is 1.1 eV. The densities of thermally generated electrons and holes in semiconductors are generally very small at room temperature given that the thermal energy, k_BT, is 26 meV at room temperature. A much larger number of conduction electrons can be introduced if desired by introducing suitable impurity atoms a process called doping the semiconductor. The purpose of semiconductor doping is to define the number and the type of free charges in a crystal region that can be moved by applying an external voltage. The electrical properties of a doped semiconductor can either be described by using the ``bond'' model or the ``band'' model. When a semiconductor is doped with impurities, the semiconductor becomes extrinsic and impurity energy levels are introduced. The bond model is used to show that a tetravalent silicon atom (group IV element) can be replaced either by a pentavalent arsenic atom (group V) or a trivalent

boron atom (group III). A semiconductor doped with impurities which are ionized (meaning that the impurity atoms either have donated or accepted an electron) will therefore contain free carriers.

Shallow impurities are impurities which require little energy - typically around the thermal energy or less - to ionize. Deep impurities require energies larger than the thermal energy to ionize so that only a fraction of the impurities present in the semiconductor contribute to free carriers. Deep impurities which are more than five times the thermal energy away from either band edge are very unlikely to ionize. Such impurities can be effective recombination centers in which electrons and holes fall and annihilate each other. Such deep impurities are also called traps. When arsenic is added to silicon, an arsenic atom with its five valence electrons forms covalent bonds with its four neighboring silicon atoms. The fifth valence electron has a relatively small binding energy to its arsenic host atom and can become a conduction electron at moderate temperature. The arsenic atom is called a donor and a donor-doped material is referred to as an n-type semiconductor. Such a semiconductor has a defined surplus of electrons in the conduction band which are the majority carriers, while the holes in the valence band, being few in number, are the minority carriers. In a similar way, if a boron atom with its three valence electrons replaces a silicon atom, an additional electron is ``accepted'' to form four covalent bonds around the boron, and a hole carrier is thus created in the valence band. Boron is referred to as an acceptor impurity and doping with boron forms a p-type semiconductor.

The dopant impurities used in controlling the conductivity type of a semiconductor usually have very small ionization energies, and hence, these impurities are often referred to as shallow impurities [16]. Naturally, the electrons tend to fill up the low energy bands first. The lower the energy, the more completely a band is filled. Semiconductors for practical applications are often doped, mainly with the aim to improve the conductivity. In metal oxide photo electrodes, shallow donors and acceptors are almost always necessary because of the low intrinsic charge carrier mobilities. The extra valence electron introduced by the donor atom is loosely bound to the donor nucleus, and can be excited to the conduction band where it then contributes to the conductivity. Conversely, holes in acceptor-type dopants can be

excited to the valence band. Since a hole is equivalent to a missing electron, one can also picture this as an electron being excited from the valence band into the energy level of the acceptor species. If the dopant level is with in $\sim 2k_BT$ of E_C or E_V, it will be (almost) fully ionized at room temperature – this is referred to as a shallow dopant. If both donor- and acceptor-like behavior is observed, the dopant is called amphoteric. Figure 1 depicts the energy band structure of a semiconductor with (a) a donor (E_d) and (b) accepter (E_d) levels. Donors add allowed electron states in the band gap close to the conduction band edge, and acceptors add allowed states just above the valence band edge. At room temperature the available thermal energy is sufficient to excite essentially all of the electrons on the donor levels into the conduction band. Similarly, holes are created when valence band electrons are thermally excited into the acceptor levels. The energies:

$$\Delta E_d = E_C - E_d \qquad \text{and} \qquad \Delta E_a = E_a - E_V, \tag{13}$$

are the respective donor and acceptor activation energies, where E_d and E_a are the energies of the donor and acceptor levels, respectively.

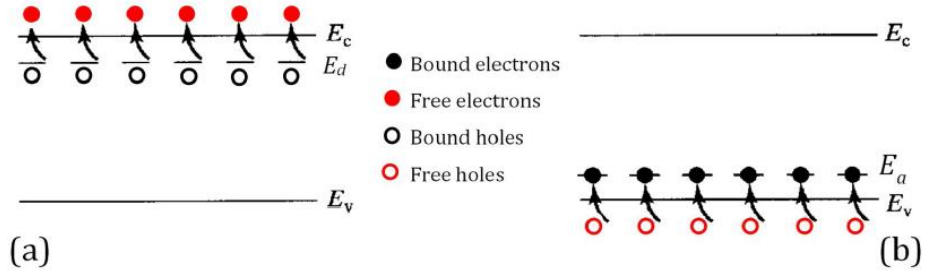

Figure 1: Thermal ionization of (a) a donor (E_d) and (b) accepter (E_a) levels [11]

As discussed above, adding donor or acceptor impurity atoms into semiconductor will change the distribution of electrons and holes in the material, and as a result, the position of the Fermi level is varied from that of the intrinsic level, so that the thermal equilibrium can be described using relations (6) and (8) or

$$n_0 = n_i \exp\left(-\frac{E_i - E_F}{k_BT}\right), \qquad p_0 = n_i \exp\left(-\frac{E_F - E_i}{k_BT}\right). \tag{14}$$

The law of mass action is derived from relations (6), (8) and (14) as:

$$n_i = \sqrt{n_0 p_0} = \sqrt{N_C N_V} \exp\left(-\frac{E_g}{2k_BT}\right). \tag{15}$$

The minority carrier density in an extrinsic semiconductor when the majority carrier density is known can be described using the law of mass action as:

$$\text{Minority carrier density} = \begin{cases} \dfrac{{n_i}^2}{p_0}, & \text{in p} - \text{type material,} \\ \dfrac{{n_i}^2}{n_0}, & \text{in n} - \text{type material.} \end{cases} \tag{16}$$

The thermal equilibrium extrinsic Fermi-level position can also be described from Eqn. (12) in terms of E_i and the thermal equilibrium carrier concentrations as:

$$E_F = E_i - k_B T \ln\left(\frac{p_0}{n_i}\right) = E_i + k_B T \ln\left(\frac{n_0}{n_i}\right). \tag{17}$$

As the charge carrier concentrations change, the position of the extrinsic Fermi energy level varies within the band gap until the system reaches thermal equilibrium. Equation (15) shows that E_F lies above E_i for n-type material $n_i > p_0$ and below E_i for p-type material $n_i < p_0$.

2.1.5 Statistics of Donors and Acceptors

The density of electrons, n_d in a shallow-donor state is: [11]

$$n_d = \frac{N_d}{1 + \frac{1}{g_d}\exp\left(\frac{E_d - E_F}{k_B T}\right)}, \tag{18}$$

where N_d the concentration of donor atoms is, g_d is the donor site degeneracy factor. The concentration of ionized donors (N_d^+) is then given by:

$$N_d^+ = N_d - n_d = \frac{N_d}{1 + g_d \exp\left(\frac{E_F - E_d}{k_B T}\right)}. \tag{19}$$

When a single donor captures an electron it becomes neutral, and when it releases an electron, it becomes positively charged. Using the same analysis for acceptors, we have:

$$N_a^- = N_a - p_a = \frac{N_a}{1 + g_a \exp\left(\frac{E_a - E_F}{k_B T}\right)}, \tag{20}$$

where p_a, the density of holes bound to acceptors, N_a the concentration of acceptor atoms, N_a^-, the concentration of ionized acceptor atoms and g_a is the acceptor site degeneracy factor. When a single acceptor captures an electron it becomes negatively charged, and neutral when it releases the electron. Most authors set g_d = 2 to account for the spin degeneracy at the donor sites (only one parabolic band at the conduction band edge). It is likewise standard practice to argue that the acceptor sites must additionally reflect the two fold (heavy- and light-hole) degeneracy of the valence band. Thus, the acceptor degeneracy factor is g_a = 2 × 2 = 4. Hence, the densities of the ionized impurities at both the donor and acceptor centers are given by:

$$N_d^+ = \frac{N_d}{1 + 2\exp\left(\frac{E_F - E_d}{k_B T}\right)} \tag{21}$$

and

$$N_a^- = \frac{N_a}{1 + 4\exp\left(\frac{E_a - E_F}{k_B T}\right)}. \tag{22}$$

At sufficiently high temperatures in p-type material, all the acceptors are ionized, so that $N_a^- \approx N_a$ or $P_a \approx 0$. This leads to the conditions $E_a - E_F \ll 0$ or $E_a \ll E_F$ resulting in the Fermi level lying above the acceptor level for p-type materials. In the same way it can be shown that complete ionization of donors for n-type materials satisfies the conditions $N_d^+ \approx N_d$ or $n_d \approx 0$ and thus $E_d \gg E_F$.

For complete freeze-out at very low temperatures in p-type material assuming zero or negligible compensation, all the acceptors are neutralized; *i.e.,* $P_a \approx N_a$ or $N_a^- \approx 0$. This again leads to the conditions $E_a - E_F > 0$ or $E_a > E_F$, with the Fermi level below the acceptor level. Similarly, for n-type materials at very low temperature, it can be shown that $n_d \approx N_d$ or $N_d^+ \approx 0$ and the Fermi level lies above the donor level ($E_d < E_F$).

2.1.6 Charge neutrality

In thermal equilibrium condition, the semiconductor crystal is electrically neutral. The electrons are distributed among the various energy states, creating negative and positive charges, but the net charge density is zero. This charge-neutrality condition is used to determine the thermal-equilibrium electrons and holes concentrations as a

function of the impurity doping concentration. A few of the donor electrons will fall into the empty states in the valence band and in doing so, will annihilate some of the intrinsic holes. The minority carrier holes concentration will therefore decrease. At the same time, because of this redistribution, the net electron concentration in the conduction band is not simply equal to the donor concentration plus the intrinsic electron concentration. We have seen that the intrinsic carrier concentration n_i is a very strong function of temperature. Under the condition of electrical neutrality the total positive charges (free holes and fixed ionized donor atom) must equal the total negative charges (free electrons and fixed ionized acceptor atoms) in a semiconductor.

Charge neutrality relationship is:

$$n_0 + N_a^- = p_0 + N_d^+. \tag{23}$$

If the concentrations of impurities are not too high, almost all of them will be ionized at room temperature. Consequently, it can be assumed that a concentration of ionized impurities equals total concentrations. In highly doped semiconductors, only a fraction of impurities replaces atoms in crystal lattice of the host semiconductor which results in part of them remaining electrically in active. Ionization energy is the energy necessary to free the fifth valance electron from the donor atom or to capture the fourth electron on to the acceptor atom. Accordingly, for the case of a donor impurity ionization equals the difference of the donor impurity level from the top of the band gap. For the case of an acceptor impurity it equals the difference of the acceptor impurity level from the bottom of the band gap [17]. From the law of mass action and charge neutrality relationship, we have:

$$p_0 = \frac{N_a^- - N_d^+}{2} + \sqrt{{n_i}^2 + \left(\frac{N_a^- - N_d^+}{2}\right)^2}. \tag{24}$$

and

$$n_0 = \frac{N_d^- - N_a^+}{2} + \sqrt{{n_i}^2 + \left(\frac{N_d^- - N_a^+}{2}\right)^2}. \tag{25}$$

For very high acceptor impurity concentrations ($N_a^- \gg N_d^+$) and ($N_a^- > n_i$), we get

$$\frac{p_0}{n_i} \approx \frac{N_a^-}{n_i} + \frac{n_i}{N_a^-} > 1, \quad \rightarrow p_0 > n_i \qquad \text{and} \qquad \frac{n_0}{n_i} \approx \frac{n_i}{N_a^-} < 1, \quad \rightarrow n_0 < n_i \tag{26}$$

From equation (23), we see that, the addition of different acceptor and donor impurity concentrations to the semiconductor increases the majority carrier concentration above the intrinsic level and decreases the minority carrier concentration below the intrinsic level. For the case when the acceptor and the donor impurity concentrations are equal (*i.e.* completely compensated material), then equation (22) becomes [18]:

$$p_o = n_0 \approx n_i. \tag{27}$$

This shows that, for completely compensated semiconductors all the carriers from donors and acceptors are involved in the recombination process. Having equal concentrations of conduction band electrons and valence band holes is a property of intrinsic semiconductors. Thermal equilibrium conditions do not allow this for a system with different donors and acceptor concentrations. A carrier generated from an impurity level can stay free provided its concentration exceeds that of oppositely charged carriers generated from another impurity in the material. If the acceptor and donor impurity concentrations are equal, the material again behaves like an intrinsic semiconductor. Equation (21) for sufficiently low temperatures yields:

$$n_0 + \frac{N_a}{1 + 4\exp\left(\frac{E_a - E_F}{k_B T}\right)} = p_0 + \frac{N_d}{1 + 2\exp\left(\frac{E_F - E_d}{k_B T}\right)}. \tag{28}$$

For p-type material, the Fermi level lies below mid-gap (closer to the valence band) as discussed earlier $E_F \ll E_d$. The exponential factor in the denominator of the last term on the right hand side of Eqn. (26) can thus be neglected for low and high temperature values. This means that almost all the donor impurities are ionized, regardless of the temperature. With this assumption, Eqn. (26) becomes:

$$n_0 + \frac{N_a}{1 + 4\exp\left(\frac{E_a - E_F}{k_B T}\right)} = p_0 + N_d. \tag{29}$$

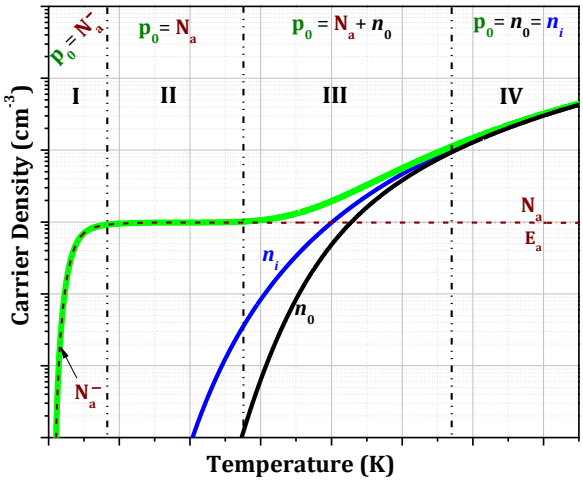

Figure 2: Temperature dependence of thermal equilibrium carrier densities for a p-type semiconductor with a shallow acceptor of doping level N_a and energy level E_a. [11]

Figure 2 illustrates the temperature dependence of thermal equilibrium carrier densities for a p-type semiconductor with a shallow acceptor of doping level N_a and energy level E_a. The graph is drawn using the simulation of the temperature dependence Hall Effect measurements along with relation (29) for the thermal equilibrium densities of different GaSb samples. The temperature variation of p_0 in Figure 2 is classified in general into four temperature regions represented by I, II, III and IV. Region I is a low temperature region and p_0 , n_0 and N_a^- all vary with temperature in region I. As a result, the intrinsic concentration n_i also varies with temperature. Due to the variation of N_a^- in region I with temperature, this region is called the partial ionization region. Since n_0 and N_d are negligibly very small for p-type semiconductor. In this region as seen from Figure 2, then we have:

$$p_0 = N_a^-. \tag{30}$$

When the temperature is increased beyond the partial ionization region, the acceptor impurity is completely ionized in region II. The temperature range in which, the acceptor level is completely ionized or region II is known as the complete ionization region. Since n_0 and N_d does not affect the majority carrier concentration in this region, p_0 remains constant and becomes:

$$p_0 = N_a. \tag{31}$$

Upon a further increase in temperature (beyond the extrinsic region), the minority carrier density, n_0 begins to affect p_0 along with N_a in region III.

$$p_0 = N_a + n_0. \tag{32}$$

Hence, region III is a transition region from extrinsic to intrinsic region. In region IV, both p_0 and n_0 approach n_i, and $N_a \ll n_i$, so that:

$$p_0 = n_0 = n_i. \tag{33}$$

The semiconductor hence enters a quasi-intrinsic region in region IV. If two acceptor levels with doping levels of N_{a1} and N_{a2} are presented in a sample, then, N_a^- in all the relations above are replaced by $N_{a1}^- + N_{a2}^-$.

2.2 Photo-response of semiconductors

The interaction of light with matter can be viewed macroscopically as consisting of four components [20] : incident, reflected, transmitted and absorbed (or scattered) components. Using the reflected, the transmitted and the absorbed (or scattered) components of photons one can describe several properties of the material. Reflectance can be defined in terms of the index of refraction of the media on either side of the surfaces (interfaces). The reflectivity and absorption depth and the scattering depth of photons in the material depend on the material and the photon energy. The photo-response of the material hence can be measured through the change in the photoconductivity due to the absorbed photons.

2.2.1 Photon absorption and free carrier generation

The term “photo-conductivity” refers to a change in conductivity of a semiconductor when illuminated by photons. The generation of excess electron-hole pairs in a semiconductor is known as the injection of excess carriers [20] . At thermal equilibrium, the valence band contains many electrons and the conduction band has many empty states into which electrons may be excited. When photons with energies equal to or greater than the band gap are incident on semiconductor materials, the photons are absorbed by the formation of electron-hole pairs. While the photo-generated carriers exist in their respective bands, they are free to contribute to the conductivity of the material. The electron-hole pairs generated by photon absorption

are known as photo-generated carriers. In the case of a pure semiconductor, photons with energy less than the band gap energy will not be enough to excite an electron from the valence band to the conduction band and it will pass through the semiconductor without being absorbed [21]. This explains why some materials are transparent in certain wave length ranges. It is possible to "see through" certain insulators, such as a good NaCl crystal, because of a large energy gap containing no or very few impurity states. The technique of measuring the absorption of incident photons is important for the determination of the band gap energy of a semiconductor. Optoelectronics is the study and application of electronic devices and systems that source detect and control light, usually considered a sub-field of photonics. In this context, light often includes invisible forms of radiation such as Γ-rays, x-rays, ultraviolet and infrared, in addition to visible light.

Optoelectronic devices are electrical-to-optical or optical-to-electrical transducers, or instruments that use such devices in their operation. Electro-optics is often erroneously used as a synonym, but is a wider branch of physics_that concerns all interactions between light and electric fields, whether or not they form part of an electronic device.

The photo-generated carriers can dominate the conduction processes in the semiconductor material. Because of the existence of two types of charge carriers in semiconductors, excess carriers can be created in the bulk without introducing any significant space charge. A large concentration of excess carriers can hence be maintained in a semiconductor under non-thermal equilibrium conditions, and this alters the conduction properties of the specimen. While the photo-generated carriers exist in their respective bands, they are free to contribute to the conductivity of the material. The photo-generated electrons and holes change the total electron and hole concentrations in the semiconductor to new values n and p, respectively, given by:

$$n = n_0 + \delta n\,, \qquad p = p_0 + \delta p \tag{34}$$

Here δn and δp are the photo-generated electron and hole concentrations, respectively. The carrier injection level in a semiconductor is determined by the concentration of excess carriers injected into it. If the non-thermal equilibrium concentration is much greater than the thermal equilibrium majority carrier

concentration ($p \gg p_0$ or $\delta p = p$) in p-type material, the system is said to be under a high injection level. Conversely, the term low injection level is a situation in which the majority carrier concentration remains essentially un perturbed($p = p_0$ or $\delta p \ll p_0$). Under non-thermal equilibrium conditions, it is often convenient to write the steady-state electron and holes concentrations in terms of the quasi-Fermi levels of electrons and holes, E_{Fn} and E_{Fp}, respectively:

$$n = n_i \exp\left(\frac{E_{Fn} - E_i}{k_B T}\right), \qquad p = n_i \exp\left(\frac{E_i - E_{Fp}}{k_B T}\right). \tag{35}$$

By multiplying these two equations gives:

$$pn = {n_i}^2 \exp\left(\frac{E_{Fn} - E_{Fp}}{k_B T}\right). \tag{36}$$

When excess carriers are injected into a semiconductor, the pn product exceeds ${n_i}^2$, so that E_{Fn} and E_{Fp} represent two separate energy levels, and $E_{Fn} > E_{Fp}$. For low injection levels, the quasi-Fermi levels become closer to the thermal equilibrium Fermi level and for high injection levels, the electron quasi-Fermi level moves closer to the conduction band and the hole quasi- Fermi level moves closer to the valence band.

2.2.2 Radiative Recombination of free carriers

Optically generated charge carriers can recombine in two different ways: radiatively or non-radiatively. Radiative recombination is the opposite of optical generation of charge carriers. It occurs when the energy of the excited electron is emitted by the formation of a photon during the annihilation of an electron pair (EHP). Non-radiative recombination occurs when excess energy of the free carriers is released as phonons or transferred as excess kinetic energy to another charge carrier. In the absence of free carriers trap, the rates of accumulation of photo-generated electron-hole in the respective bands are equal and always given by the difference between the optical generation, G_0 and the net recombination rate of photo-generated carriers, U as [11] :

$$\frac{d\delta n}{dt} = \frac{d\delta p}{dt} = G_0 - U. \tag{37}$$

Radiative recombination is a direct recombination mechanism, in which the electrons in the conduction band decay to the valence band (*i.e.* recombine with holes in the valence band). This is a very efficient process in direct band gap semiconductors. The energy lost by an electron in making the transition is released as a photon. The net radiative recombination rate, U_R is directly proportional to union of the product of the concentration of photo-generated electrons in the conduction band with available holes in the valence band, $\delta n(p_0 + \delta p)$ and the product of the concentration of photo-generated holes in the valence band with available holes in the valence band, $\delta p(n_0 + \delta n)$:

$$U_R = C_R\,(n_0\delta p + p_0\delta n + \delta p\delta n), \tag{38}$$

where C_R is a constant known as the coefficient of holes in the valence band for the capture of electrons, and is related to the electron capture cross-section σ_R and the thermal velocity of the electrons ϑ_{th} :

$$C_R = \sigma_R\,\vartheta_{th}. \tag{39}$$

The capture cross-section, σ_R can be thought of as the volume swept out per unit time by a particle. When the dispersion in the dielectric constant is ignored, the band-to-band capture coefficient for bands with spherical symmetry was shown by van Roosbroeck and Shockley to depend on the absorption coefficient through the relation

$$C_R = e\pi\sqrt{k_\infty}\left(\frac{m_n}{m_n^* + m_p^*}\frac{300}{T}\right)^{3/2}\left(1 + \frac{m_n}{m_n^*} + \frac{m_n}{m_p^*}\right)\left(E_g^2 + 3k_BT + 3.75k_B^2\,T^2\right). \tag{40}$$

Since $E_g \gg k_BT$, the term E_g^2 is dominant in large band gap materials. At steady-state the rate of accumulation of carriers is zero, so that:

$$\frac{d\delta n}{dt} = G_0 - U = \frac{d\delta p}{dt} = 0. \tag{41}$$

In the absence of free carriers trap $\delta n = \delta p$ and hence:

$$G_0 = U = \frac{\delta n}{\tau_R} = C_R(n_0 + p_0 + \delta n)\delta n. \tag{42}$$

where τ_R is called the radiative excess carrier recombination lifetime. The general form for the radiative recombination lifetime is then given by:

$$\tau_R = \frac{\delta n}{U_R} = \frac{1}{C_R(n_0 + p_0 + \delta n)}. \quad (43)$$

When $\delta n = G_0\tau_R$ in relation (41) is substituted into relation (42), we get:

$$\tau_R = \frac{2\tau_{R0}\tau_k}{\tau_{R0} + \tau_k}, \quad (44)$$

where

$$\tau_{R0} = \frac{1}{C_R(n_0 + p_0)} \quad \text{and} \quad \tau_k = \frac{\tau_{R0}}{\sqrt{1 + 4C_R G_0 \tau_{R0}^2}}. \quad (45)$$

At intrinsic level when $n_0 = p_0 = n_i$

$$\tau_{Ri} = \frac{1}{2C_R n_i} \quad \text{and} \quad \tau_R = \frac{2\tau_{Ri}\tau_{ki}}{\tau_{Ri} + \tau_{ki}}. \quad (46)$$

where

$$\tau_{ki} = \frac{\tau_{Ri}}{\sqrt{1 + 4C_R G_0 \tau_{Ri}^2}}. \quad (47)$$

For low injection level, $G_0 \to 0$, we have for extrinsic semiconductor that:

$$\tau_k = \tau_{R0} \quad \text{and} \quad \tau_R = \tau_{R0} \quad (48)$$

and for high injection level, $\tau_k \ll \tau_{R0}$,

$$\tau_R = 2\tau_k. \quad (49)$$

For intrinsic semiconductor the low injection case when $G_0 \to 0$ is:

$$\tau_{ki} = \tau_{Ri} \quad \text{and} \quad \tau_R = \tau_{Ri} \quad 50)$$

and the corresponding high injection level when $\tau_{ki} \ll \tau_{Ri}$,

$$\tau_R = 2\tau_{ki}. \quad (51)$$

Chapter Three

Methodology

The primary task on this work was to select an appropriate semiconductor sample in which deep and shallow level impurities dominate the electrical properties that were GaSb. The electrical and optical properties of GaSb were studied through literature reviews. Literature research consists of physics journal articles on the subject matter through a search of online library. In addition, the hand book of physical science and physics were used as a primary reference for much of the initial information. Following the literature review, we collected 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 ionized acceptor for different energy levels (deep and shallow) were described as function of temperature. This also helps to describe the entire majority carrier concentration (ionized acceptors plus intrinsic concentration) as function of temperature. The graphs were drawn using the simulation of the temperature dependence Hall Effect measurements for the thermal equilibrium densities of different GaSb samples by varying temperature, doping density and acceptor level energies and also the intrinsic density n_i could be described. The minority carrier density n_0 was determined using the law of mass action. This also helps to describe the entire majority carrier concentration (ionized acceptors plus intrinsic concentration) as function of temperature.

When this data was used along with the statistics that were describing the excess carrier lifetime in the entire bulk of the semiconductor, the contributions of deep and shallow acceptors to the radiative excess carrier lifetime in GaSb samples with various doping levels were investigated at different temperature ranges. The radiative excess carrier lifetimes were described and the resulting temperature dependence of radiative excess minority carrier lifetime is hence the combined effects of the injection level of the illumination, G_0 and temperature dependences of the radiative capture coefficient, C_R and the thermal equilibrium carrier concentrations.

Chapter four

Results and Discussion

Under this topic, the effects of the deep versus shallow acceptors on the thermal and electrical properties of a direct band gap GaSb semiconductor is described and discussed in detail. First, the effects of deep versus shallow acceptors on the thermal equilibrium properties of GaSb, especially on the thermal equilibrium carrier concentration is investigated in detail. Then, the effects of deep versus shallow acceptors on the performance of GaSb, especially the effects that deep versus shallow acceptors have on the radiative excess carrier lifetimes is described.

4.1 Temperature dependence of thermal equilibrium

Majority carrier density

In this section, the effects of deep and shallow acceptors on the thermal equilibrium carrier concentration of samples with various doping levels are investigated at different temperature ranges. The graphs are drawn using the simulation of the temperature dependence Hall Effect measurements along with relation (29) for the thermal equilibrium densities of different GaSb samples by varying temperature, doping density and acceptor level energies as discussed in subsection 2.1.6 above. The intrinsic density n_i can be described using relations (11) or (15). The minority carrier density n_0 is determined using the law of mass action, relation (16).

4.1.1 Acceptors with different energies and equal doping densities

Figure 3 illustrates the temperature dependence of thermal equilibrium carrier concentration of three different GaSb samples with equal doping densities of 10^{17} cm^{-3} and different acceptor level energies of (a) 10 meV, (b) 150 meV and (c) 350 meV. The intrinsic carrier density, n_i is represented by blue solid line, the majority carrier density, p_0 is represented by green bold line, the minority carrier density, n_0 is

represented by black solid line and the ionized acceptor, N_a^- is represented by brown broken line. As one can see from Figure 3 (a) to (c), when the doping level of each acceptor level is kept constant and the energies of the acceptor levels are varying, the temperature ranges of the thermal equilibrium carrier concentration discussed in Figure 2 above vary in different fashions.

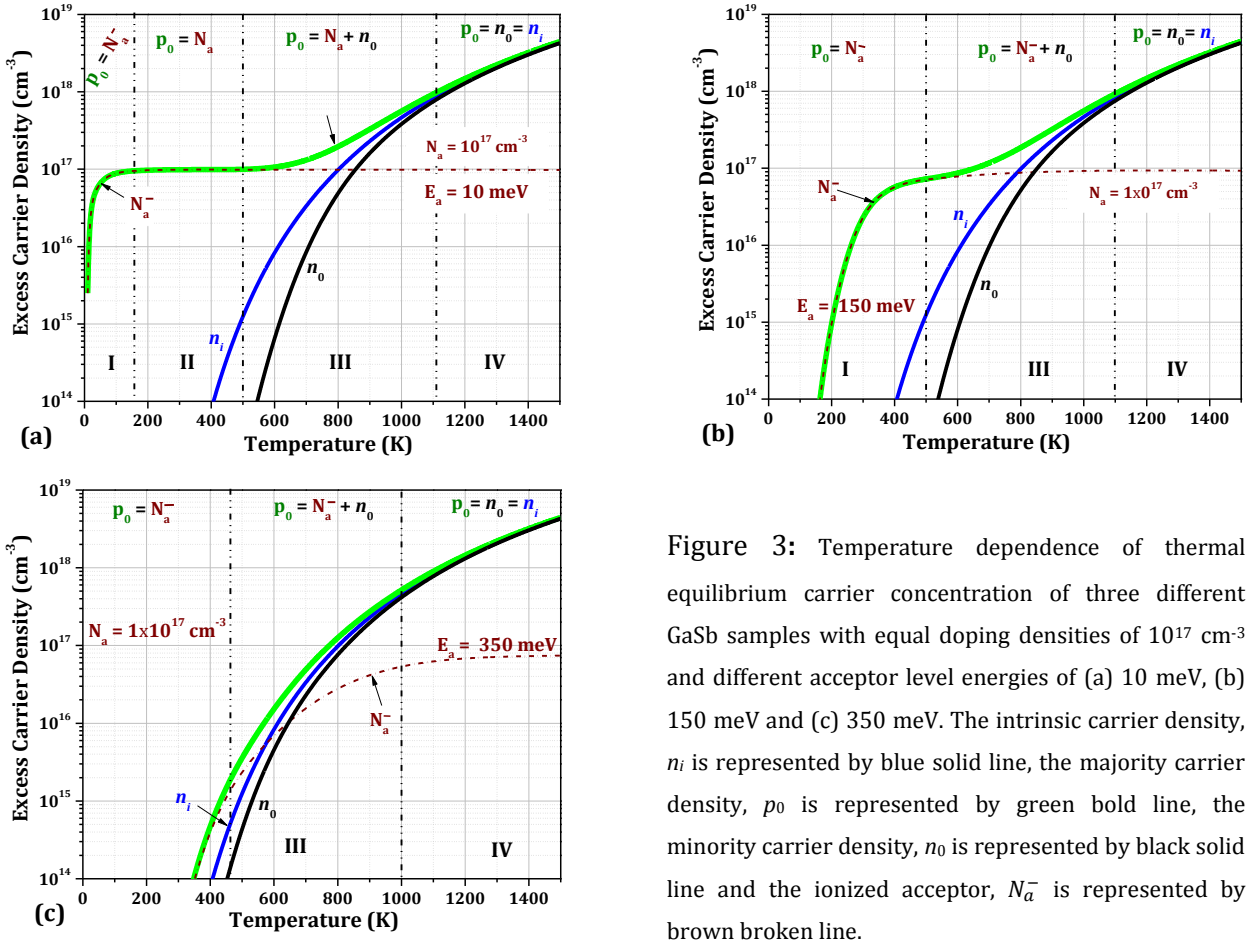

Figure 3: Temperature dependence of thermal equilibrium carrier concentration of three different GaSb samples with equal doping densities of 10^{17} cm^{-3} and different acceptor level energies of (a) 10 meV, (b) 150 meV and (c) 350 meV. The intrinsic carrier density, n_i is represented by blue solid line, the majority carrier density, p_0 is represented by green bold line, the minority carrier density, n_0 is represented by black solid line and the ionized acceptor, N_a^- is represented by brown broken line.

In Figure 3 (a) where the acceptor level is very shallow, very narrow partial ionization region (region I), sufficiently large completely ionization region (region II), transition to intrinsic region (region III) and quasi intrinsic region (region IV) exist. The decrease in the ionization of the acceptors in the lower temperature region of region I is called acceptors freeze-out. As the acceptor level goes deep into the forbidden gap as in Figure 3(b), the partial ionization region (region I) becomes very wider and starts to dominate the entire low temperature regime and the completely ionization region (region II) diminishes to zero. This shows that, as the acceptors goes

deep into the forbidden gap, freeze-out of carriers also increases. The transition to intrinsic and quasi intrinsic regions (regions III and IV) in this case remain unaffected by the slight change of acceptor level. As the acceptor level approaches the middle of the forbidden gap as shown in Figure 3(c), both p_0 and n_0 approach the intrinsic concentration, n_i in the higher temperature regime and the partial ionization is limited to only the very low temperature regime. Increasing the deepness of the acceptor level in general decreases the majority carrier concentration and increases the minority carrier concentrations in region I.

From the description of Figure 3 above, variation of the energies of the acceptor levels mainly affects only the partially ionization and completely ionization region (regions I and II) of the temperature variation of the thermal equilibrium carrier density. The contribution of shallow level acceptors to the thermal equilibrium carrier density is very high as compared to the deep level acceptors of the same impurity concentration. Very deep acceptors have very little contributions to the thermal equilibrium carrier concentrations as shown in Figure 3(c).

4.1.2 Shallow acceptors with the same energies and different doping densities

Figure 4 depicts the temperature dependence of thermal equilibrium carrier concentration in GaSb samples of shallow acceptor level energies of 20 m eV and doping densities of (a) 10^{17} cm^{-3}, (b) 10^{18} cm^{-3} and (c) 3×10^{19} cm^{-3}. In the same way as inFigure 4, n_i, p_0, n_0 and N_a^- in this case are also represented by blue solid line, green bold line, black solid line and brown broken line, respectively.

In addition to the variation in the magnitude of the thermal equilibrium carrier concentration, varying the doping concentration of a shallow level also has other various effects on the temperature dependence of the thermal equilibrium carrier concentrations. Some of these effects are described in Figure 4 (a) to (c). For a slightly doped sample with a shallow acceptor as the one in Figure 4 (a), all the four temperature regions discussed in Figure 2 above exist within the relatively low temperature ranges.

A slight increase in the acceptor doping level by keeping the energy level constant, leads to the widening of the completely ionization region (region II) and the shifting of the transition region to the intrinsic region (region III) and the quasi intrinsic region (region IV) to the high temperature regions as depicted inFigure 4 (b). The temperature range of partially ionization region (region I) is unaffected by the change in the doping density. For a highly doped shallow acceptor, still the width of the partially ionization region (region I) remains unaffected, the width of the completely ionization region (region II) increases to very high temperature range, the transition region to the intrinsic region (region III) and the quasi intrinsic region (region IV) are shifted to very high temperature region as shown in Figure 4(c).

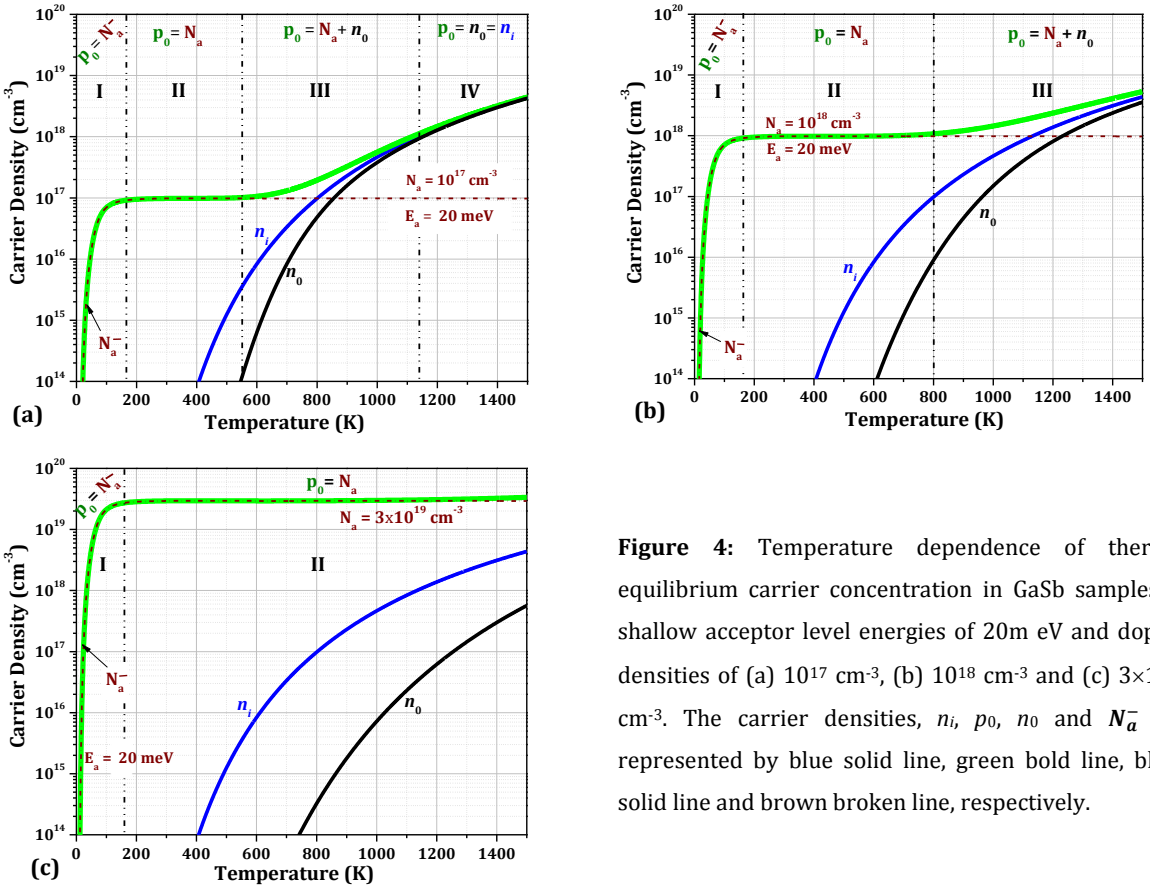

Figure 4: Temperature dependence of thermal equilibrium carrier concentration in GaSb samples of shallow acceptor level energies of 20m eV and doping densities of (a) 10^{17} cm^{-3}, (b) 10^{18} cm^{-3} and (c) 3×10^{19} cm^{-3}. The carrier densities, n_i, p_0, n_0 and $\boldsymbol{N_a^-}$ are represented by blue solid line, green bold line, black solid line and brown broken line, respectively.

In a sample slightly doped with a shallow acceptor, the extrinsic property dominates only the low temperature regime and the intrinsic property dominates the high temperature regime as in Figure 4 (a). In a sample highly doped with a shallow

acceptor, the extrinsic property dominates almost all the entire temperature regime as shown in Figure 4 (c).

4.1.3 Presence of both deep and shallow acceptors in a single material

Figure 5 describes the temperature dependence of thermal equilibrium carrier concentration in GaSb samples and the contributions of a shallow and a deep acceptor levels of energies 10 meV and 220 meV, respectively, for the case when the shallow acceptor level has (a) smaller doping density than the deep level, (b) equal doping density to the deep level and (c) larger doping density than the deep level. In Figure 5 (a), when the shallow acceptor level has smaller doping density than the deep level, the partially ionized and the completely ionized region of the shallow level dominates the low temperature regime and the partially ionized region of the deep level dominates the higher temperature regime below the quasi-intrinsic region. When the shallow acceptor level has equal doping density to the deep level as in the case of Figure 5 (b), again, the partially ionized and the completely ionized region of the shallow level dominates the low temperature regime and the combined effects of the partially ionized region of the shallow level and the completely ionized region of the deep levels dominates the higher temperature regime below the quasi-intrinsic region. For the case when the shallow acceptor level has larger doping density than the deep level as in the case of Figure 5 (c), the shallow level dominates the entire temperature regime below the quasi-intrinsic region and the deep level has no contribution in this case. In the presence of shallow and deep levels in a sample, the deep level can have contribution to the thermal equilibrium carrier concentration if it has larger doping concentration than the shallow levels as in Figure 5 (a) and (b), while the shallow level dominates the low temperature regime when it has smaller doping density than the deep levels as in Figure 5 (a) and dominates the entire temperature range below the quasi-intrinsic region when it has larger density than the deep levels as Figure 5 (c).

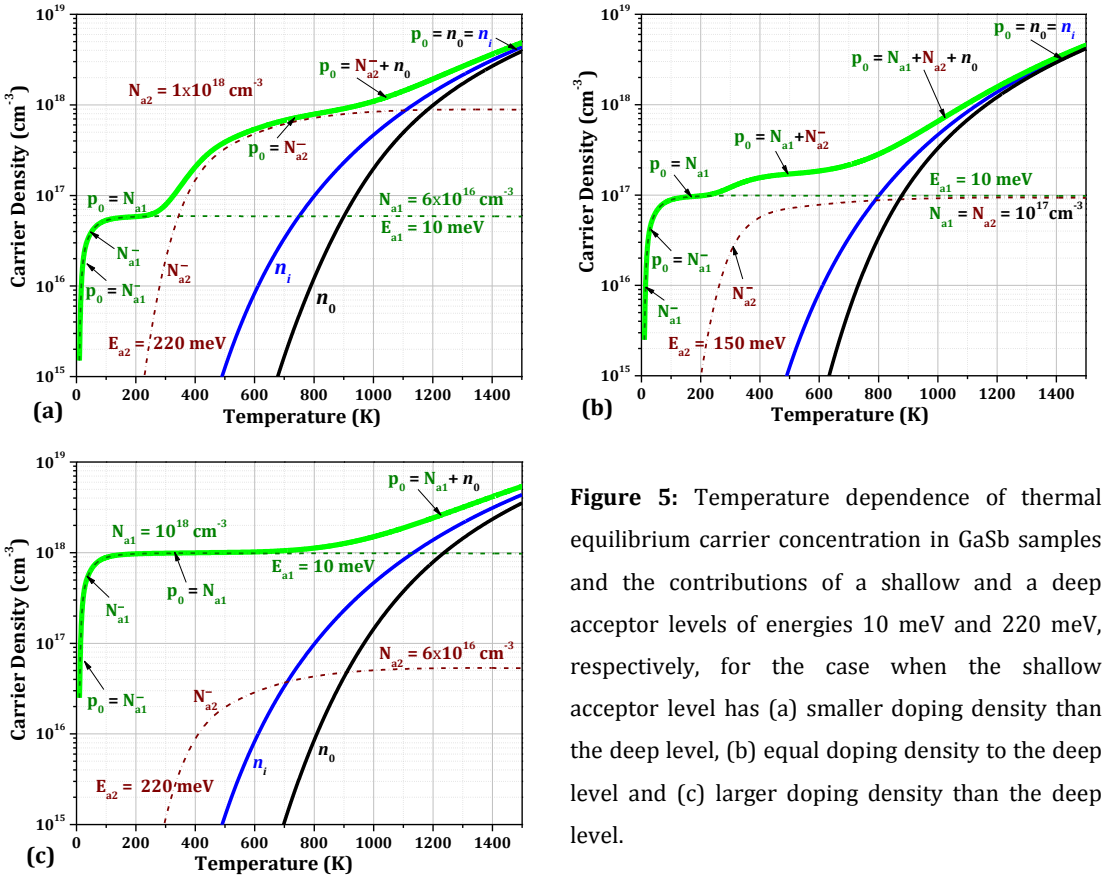

Figure 5: Temperature dependence of thermal equilibrium carrier concentration in GaSb samples and the contributions of a shallow and a deep acceptor levels of energies 10 meV and 220 meV, respectively, for the case when the shallow acceptor level has (a) smaller doping density than the deep level, (b) equal doping density to the deep level and (c) larger doping density than the deep level.

Next, the effects of deep versus shallow acceptors on the radiative excess carrier lifetime are investigated.

4.2 Temperature dependence of radiative excess carrier lifetimes

Under this section, the contributions of deep and shallow acceptors to the radiative excess carrier lifetime in GaSb samples with various doping levels are investigated at different temperature ranges. The radiative excess carrier lifetimes are described using relations (44) to (51) discussed in subsection 2.2.2 above. The resulting temperature dependence of radiative excess minority carrier lifetime is hence the combined effects of the injection level of the illumination, G_0 and temperature dependences of the radiative capture coefficient, C_R and the thermal equilibrium carrier concentrations (especially the majority carrier concentration, p_0).

4.2.1 Acceptors with equal energy levels and different doping densities (Low injection level)

Figure 6 illustrates the temperature dependence of low injection level radiative excess carrier lifetimes in three GaSb samples with shallow acceptor levels of equal energies of 20 meV and different doping levels of (a) 10^{15} cm^{-3}, (b) 10^{17} cm^{-3} and (c) 10^{19} cm^{-3}. The intrinsic radiative excess carrier lifetime, τ_{Ri} is represented by blue solid line and the extrinsic radiative excess carrier life time, τ_R is represented by a green bold line. As can be seen from Figure 6, the extrinsic radiative excess carrier lifetime due to a shallow acceptor always dominates the low temperature regime and the intrinsic radiative excess carrier lifetime dominates the higher temperature regime. The temperature ranges of the extrinsic radiative excess carrier lifetime in Figure 6 can also be classified into three regions represented by Roman numbers I, II and III.

Region I is a very low temperature region where carriers freeze-out takes place in the shallow acceptor levels. This region covers the most part of the partially ionized acceptor region discussed in section 4.1. Even though, the radiative carrier capture coefficient decreases throughout the whole temperature range with increasing temperature, its product with the thermal equilibrium carrier concentration decreases in region I. As a result, the low injection level extrinsic radiative excess carrier lifetime described by relation (45) increases with decreasing temperature in region I. Hence, the extrinsic radiative excess carrier lifetime is very high in the lower temperature regime of region I due to carriers freeze-out.

Region II also covers some parts of the partially ionized acceptors region, the entire part of the completely ionized acceptors region and some part of the transition to the intrinsic region discussed in section 4.1 above. As already discussed in section 4.1, the thermal equilibrium majority carrier concentration almost remains constant in this region. However, the product of the radiative free carrier capture coefficient with the carrier concentration decreases with increasing temperature in this region. As a result, the extrinsic radiative excess carrier lifetime slightly increases with increasing temperature in region II.

Region III covers some part of the transition to the intrinsic region and the entire part of the quasi-intrinsic region discussed in section 4.1 above. The product of the radiative free carrier capture coefficient with the carrier concentration increases with increasing temperature in region III. This results in the slight decrease of the extrinsic radiative excess carrier lifetime with increasing temperature in region III. Hence, region III shows fully intrinsic property.

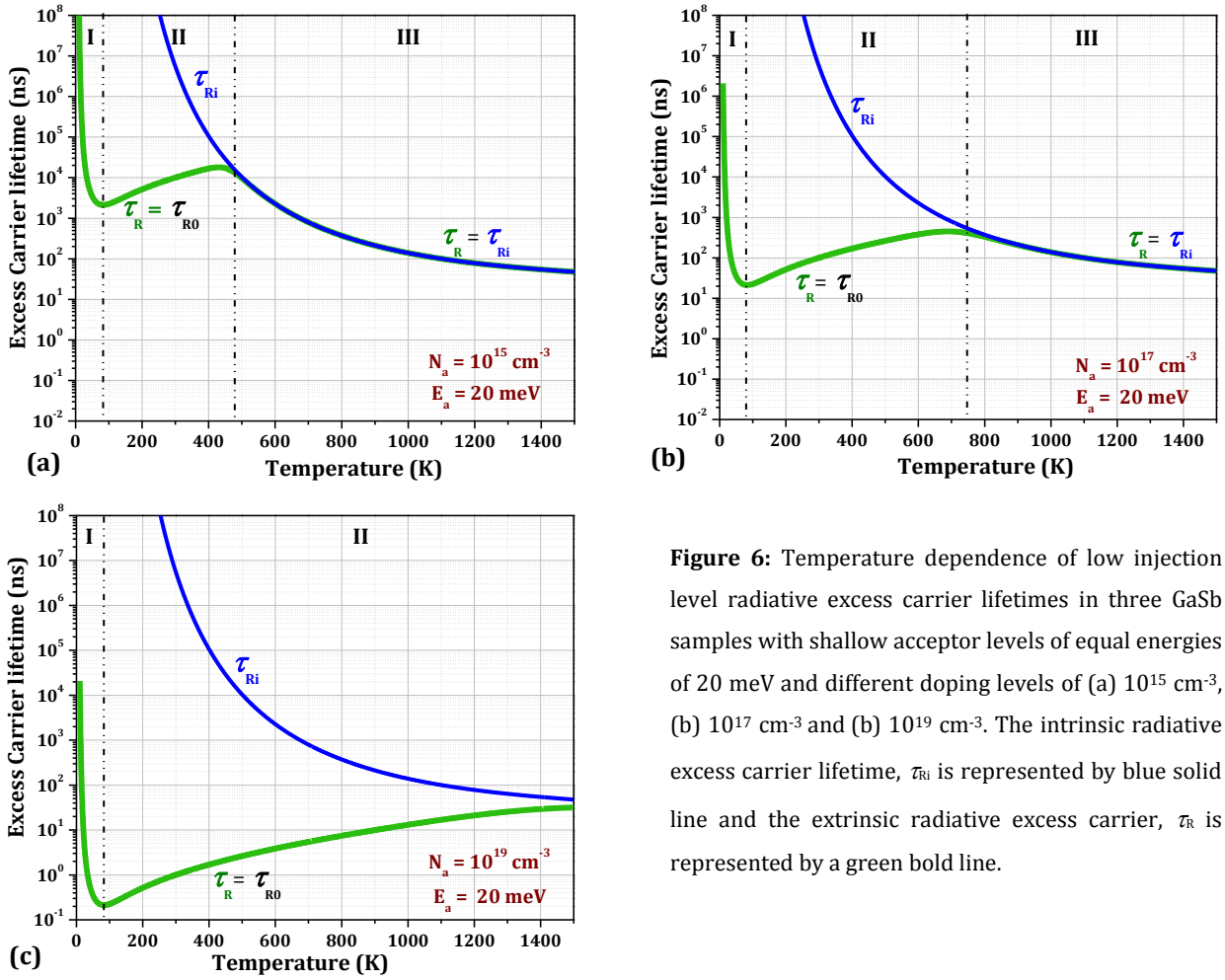

Figure 6: Temperature dependence of low injection level radiative excess carrier lifetimes in three GaSb samples with shallow acceptor levels of equal energies of 20 meV and different doping levels of (a) 10^{15} cm^{-3}, (b) 10^{17} cm^{-3} and (b) 10^{19} cm^{-3}. The intrinsic radiative excess carrier lifetime, τ_{Ri} is represented by blue solid line and the extrinsic radiative excess carrier, τ_R is represented by a green bold line.

Variation of the doping level does not affect the temperature range of freeze-out zone (region I), whereas the temperature of region II increases due to the increase in the temperature range of the completely ionized region and region III is shifted to the very high temperature region with increasing the doping level as depicted inFigure 6 (a) to (c). Note that, variation of the doping level does not affect the boundary between regions I and II, whereas the boundary between regions II and III is shifted to high

temperature region. Increasing the doping density in general decreases the magnitude of the extrinsic radiative excess carrier lifetime as depicted Figure 6 (a) to (c).

4.2.2 Different acceptor levels and a single acceptor density (low injection level)

Figure 7 shows the temperature dependence of radiative excess carrier lifetimes in GaSb samples with doping levels 10^{17} cm^{-3} and acceptor level energies of (a) 20 meV, (b) 100 meV and (c) 300 meV. The intrinsic and extrinsic radiative excess carrier lifetime, τ_{Ri} and τ_R are represented by blue solid line and green bold line, respectively. The temperature range of region I also increases and that of region II decreases with increasing the depth of the energy of the acceptor level as depicted in Figure 7 (a) and (b) and as the energy of the acceptor level approaches the center of the band gap, region II diminishes to zero and the extrinsic radiative excess carrier lifetime approaches that of intrinsic radiative excess carrier lifetime as shown in Figure 7(c). However, the temperature range of the quasi-intrinsic region is not affected by the variation of the energy of the acceptor level. Note that, variation of the acceptor energy level does not affect the boundary between regions II and III, whereas the boundary between regions I and II is shifted to high temperature region with increasing the depth of the acceptor energy level.

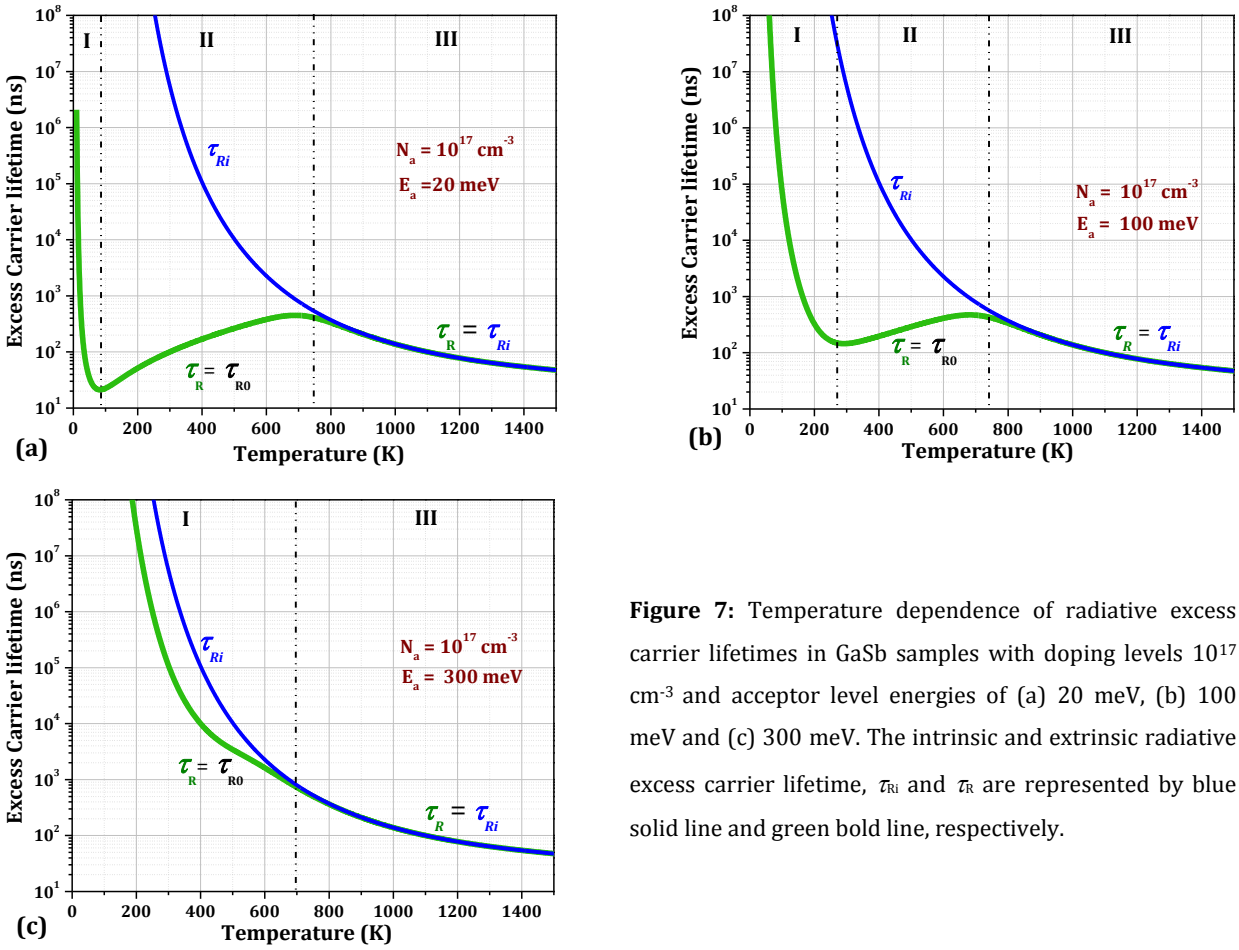

Figure 7: Temperature dependence of radiative excess carrier lifetimes in GaSb samples with doping levels 10^{17} cm^{-3} and acceptor level energies of (a) 20 meV, (b) 100 meV and (c) 300 meV. The intrinsic and extrinsic radiative excess carrier lifetime, τ_{Ri} and τ_R are represented by blue solid line and green bold line, respectively.

As the depth of the acceptor level increases, the magnitude of the extrinsic radiative excess carrier lifetime in general increases slightly due to the increase in the carriers freeze-out as depicted in Figure 7 (a) to (c).

4.2.3 Presence of ashallow and deep acceptors in a material (Low injection level)

Figure 8 depicts the temperature dependence of extrinsic radiative excess carrier lifetimes in GaSb samples with two acceptor levels of energies of 10 meV and 300 meV each and respective doping concentrations of (a) 10^{16} cm^{-3} and 10^{19} cm^{-3}, (b) 10^{16} cm^{-3} and 10^{18} cm^{-3} and (c) 10^{18} cm^{-3} and 10^{16} cm^{-3}. The excess carrier lifetime due to the contribution of the shallow acceptor level is represented by τ_1 and that of the deep level is represented by τ_2. The combined effect of the excess carrier lifetime (effective excess carrier lifetime) due to both the shallow and deep acceptor levels is represented by τ_{eff}.

For a sample in Figure 8 (a), the photo-response of a slightly doped shallow acceptor level of energy 10 meV and doping density of 10^{16} cm^{-3}, τ_1 is competing with the photo-response of a highly doped deep acceptor level of energy 300 meV and doping density of 10^{19} cm^{-3}, τ_2. The photo-response of the shallow level, τ_1 in this case dominates very small ranges of the lower temperature regime and the photo-response of the deep acceptor, τ_2 dominates very large ranges of the higher temperature regime below the quasi-intrinsic temperature region as depicted in Figure 8 (a). The lower boundary of the temperature range of the quasi-intrinsic region is shifted to very high temperature regime.

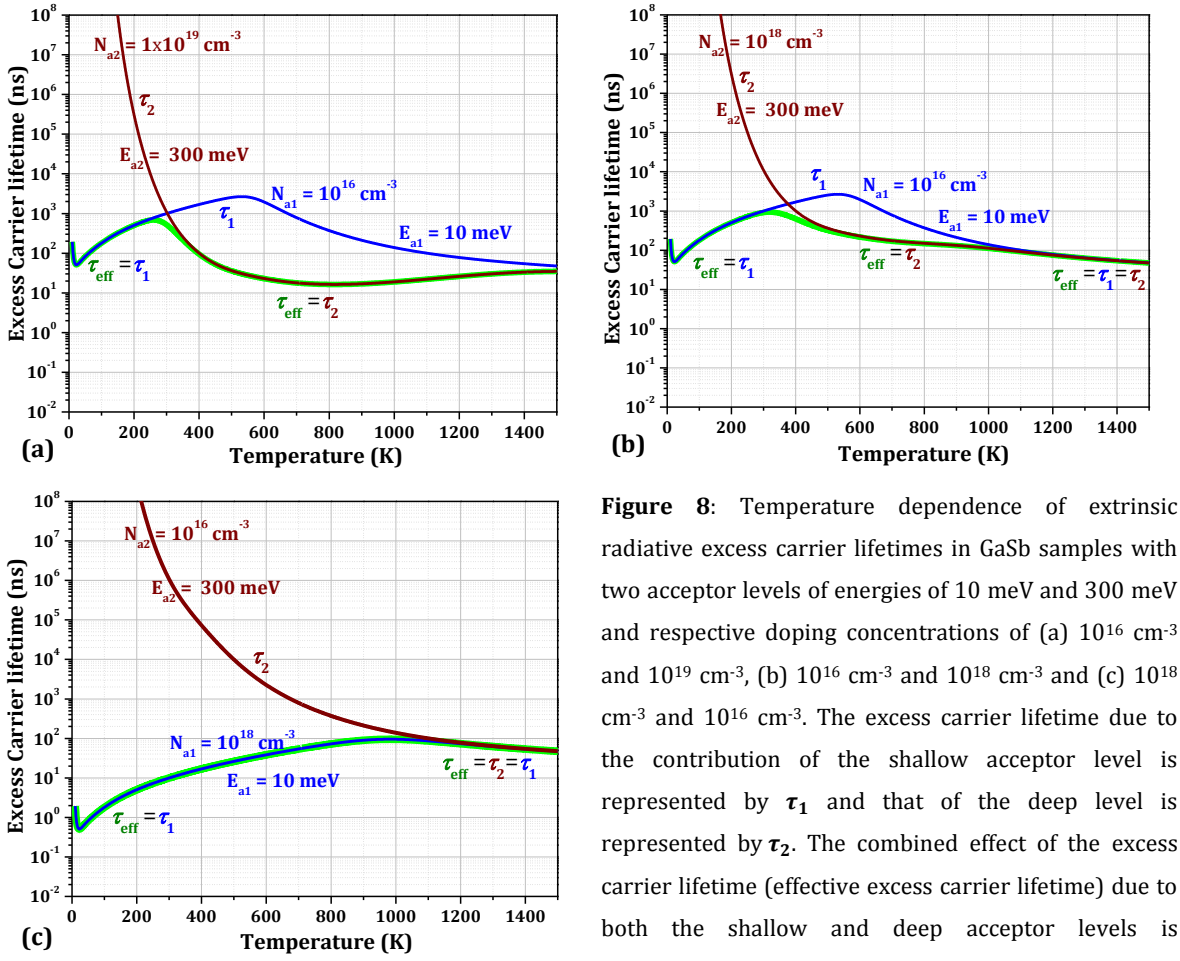

Figure 8: Temperature dependence of extrinsic radiative excess carrier lifetimes in GaSb samples with two acceptor levels of energies of 10 meV and 300 meV and respective doping concentrations of (a) 10^{16} cm^{-3} and 10^{19} cm^{-3}, (b) 10^{16} cm^{-3} and 10^{18} cm^{-3} and (c) 10^{18} cm^{-3} and 10^{16} cm^{-3}. The excess carrier lifetime due to the contribution of the shallow acceptor level is represented by $\boldsymbol{\tau_1}$ and that of the deep level is represented by $\boldsymbol{\tau_2}$. The combined effect of the excess carrier lifetime (effective excess carrier lifetime) due to both the shallow and deep acceptor levels is represented by $\boldsymbol{\tau_{eff}}$.

For a sample in Figure 8 (b), again, the photo-response of a slightly doped shallow acceptor level described in (a) is competing with the photo-response of relatively low doping deep acceptor level of energy 300 meV and doping density of 10^{18} cm^{-3} as

compared to the deep accepter level in (a). As can be seen from Figure 8 (b), the photo-response of the shallow level, τ_1 in this case dominates relatively larger ranges of the lower temperature regime and the photo-response of the deep acceptor, τ_2 also dominates relatively smaller ranges of the higher temperature regime below the quasi-intrinsic temperature region as depicted in Figure 8 (a). The lower boundary of the temperature range of the quasi-intrinsic region in this case is lowered to lower temperature regime.

Finally, in a sample in Figure 8 (c), the photo-response, τ_1 of a highly doped shallow acceptor level of energy 10 meV and doping density of 10^{18} cm^{-3} is competing with the photo-response, τ_2 of a slightly doped deep acceptor level of energy 300 meV and doping density of 10^{16} cm^{-3}. The photo-response of the shallow level, τ_1 in this case dominates all the temperature ranges below the quasi-intrinsic region and the photo-response of the deep acceptor, τ_2 has no any effect on the photo-response of the sample.

Therefore, based on the descriptions of Figure 8 above, the following very important three conclusions can be drawn. These are, when two acceptors one shallow and the other deep are presented in a semiconductor sample;

1. the photo-response of the shallow level always dominates the lower temperature ranges (see Figure 8 (a) to (c)),
2. the photo-response of the deep level can dominate some temperature ranges below the quasi-intrinsic region only when its doping level is greater than that of the shallow level (see Figure 8 (a) and (b)),
3. the photo-response of the deep level has no any effect on the photo-response of the sample, when its doping level is less than that of the shallow level (see Figure 8 (c)).

4.2.4 Different injection levels versus different acceptor levels

Figure 9 illustrates the temperature dependence of radiative excess carrier lifetimes in GaSb samples with acceptor levels of doping concentrations 10^{19} cm^{-3} each, respective energies of (a) 15 meV, (b) 50 meV, (c) 200 meV; and when they are all subjected to illuminations of absorption rates 10^{15} $cm^{-3}s^{-1}$, 10^{20} $cm^{-3}s^{-1}$, 10^{24} $cm^{-3}s^{-1}$ and

10^{26} $cm^{-3}s^{-1}$. The low injection level excess carrier lifetimes are represented by the blue solid lines, the excess carrier lifetimes with an illumination of absorption rate of 10^{15} $cm^{-3}s^{-1}$ is represented by a wine solid line, that with an illumination of absorption rate of 10^{20} $cm^{-3}s^{-1}$ is represented by an olive solid line, the one with an illumination of absorption rate of 10^{24} $cm^{-3}s^{-1}$ is represented by an orange line and that with an illumination of absorption rate of 10^{26} $cm^{-3}s^{-1}$ is represented by a dark yellow line. The case when the effective excess carrier lifetime is less than the low injection excess carrier lifetime (blue line) is said to be high injection level excess carrier lifetime. A sample with a very shallow acceptor as the one in Figure 9 (a) is under low injection level for all of the illuminations with absorption rates less than 10^{21} $cm^{-3}s^{-1}$. For the illuminations with absorption rates between 10^{21} $cm^{-3}s^{-1}$ and 10^{24} $cm^{-3}s^{-1}$, the system remains under low injection level in the partially ionized region (region I) and in the higher temperature ranges of the quasi-intrinsic region (region IV), whereas, The completely ionized region (region II) and the lower temperature ranges of the quasi-intrinsic region (region IV) remains under high injection. For an illuminations with absorption rates greater than 10^{24} $cm^{-3}s^{-1}$, all the regions including the lower temperature ranges of the quasi-intrinsic region (region IV) remain under high injection as depicted in Figure 9 (a).

As the acceptor level goes deep into the forbidden energy gap as in Figure 9 (b) and (c), the lower temperature regions become high injection regions for the illuminations of absorption rates less than 10^{24} $cm^{-3}s^{-1}$. As the depth of the acceptor level approaches the mid gap, the high injection level condition for the illuminations with absorption rates less than 10^{24} $cm^{-3}s^{-1}$ extends to high temperature regions depending on the magnitude of the absorption rates as depicted in Figure 9(c). Illuminations with high absorption rate are extended more into the higher temperature region than the one with less absorption rate.

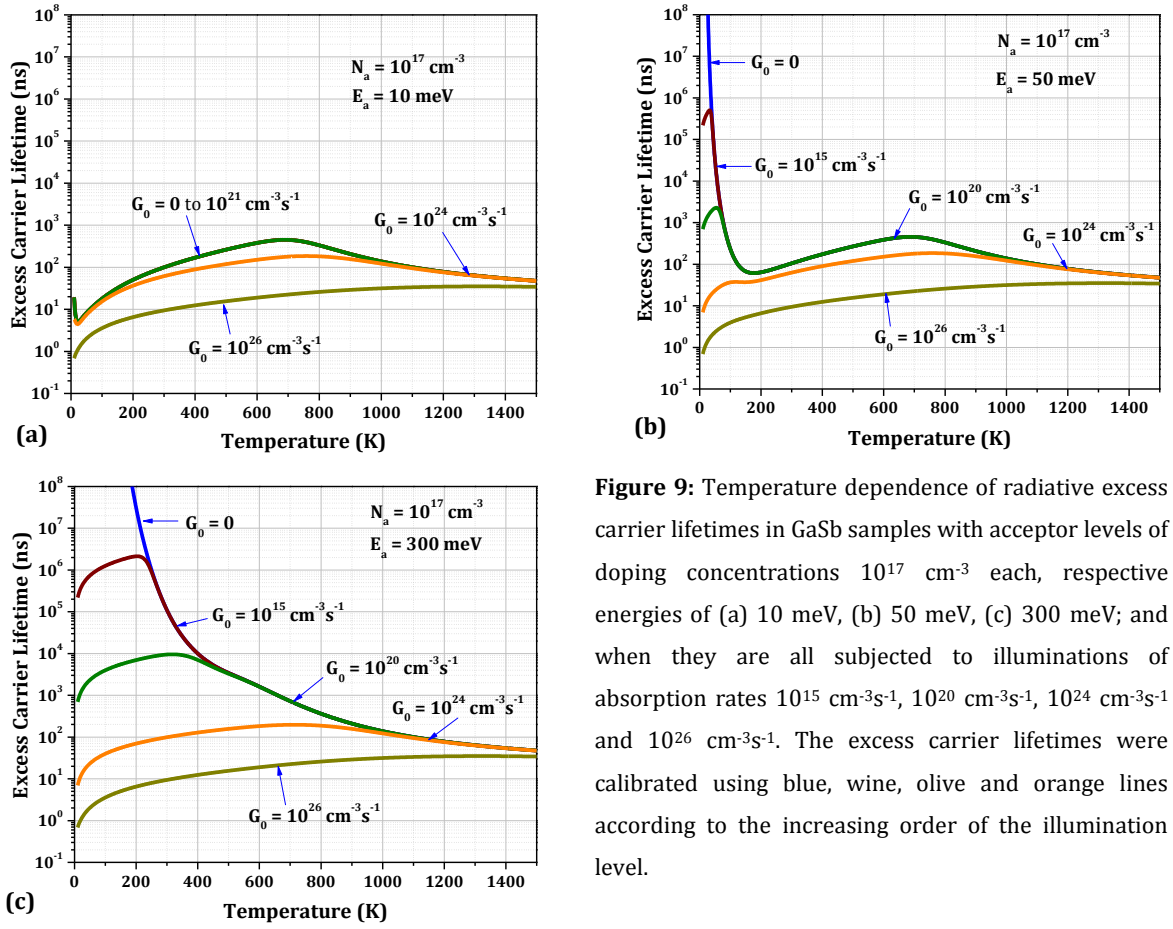

Figure 9: Temperature dependence of radiative excess carrier lifetimes in GaSb samples with acceptor levels of doping concentrations 10^{17} cm^{-3} each, respective energies of (a) 10 meV, (b) 50 meV, (c) 300 meV; and when they are all subjected to illuminations of absorption rates 10^{15} cm^{-3}s^{-1}, 10^{20} cm^{-3}s^{-1}, 10^{24} cm^{-3}s^{-1} and 10^{26} cm^{-3}s^{-1}. The excess carrier lifetimes were calibrated using blue, wine, olive and orange lines according to the increasing order of the illumination level.

Therefore, it can be concluded from Figure 9 that, shallow acceptors are less sensitive to the low injection level illuminations as compared to the deep acceptor levels. The photo-responses of semiconductors with deep acceptors are very sensitive at very low temperature regimes. This is why most of the semiconductor photo detectors are working only at very low temperature regions [11].

Chapter five

Conclusion

In this study the effects of deep versus shallow acceptors on the thermal equilibrium properties of GaSb; especially on the thermal equilibrium carrier concentration is investigated in detail. Then, the effects of deep versus shallow acceptors on the performance of GaSb, especially the effects that deep versus shallow acceptors have on the radiative excess carrier lifetimes is described. Variation of the energies of the acceptor levels mainly affects only the partially ionization and completely ionization region of the temperature variation of the thermal equilibrium carrier density. The contribution of shallow level acceptors to the thermal equilibrium carrier density is very high as compared to the deep level acceptors of the same impurity concentration. Very deep acceptors have very little contributions to the thermal equilibrium carrier concentrations. In a sample slightly doped with a shallow acceptor, the extrinsic property dominates only the low temperature regime and the intrinsic property dominates the high temperature regime and highly doped with a shallow acceptor, the extrinsic property dominates almost all the entire temperature regime.In addition to this in the presence of shallow and deep levels in a sample, the deep level can have contribution to the thermal equilibrium carrier concentration if it has larger doping concentration than the shallow levels, while the shallow level dominates the low temperature regime when it has smaller doping density than the deep levels and dominates the entire temperature range below the quasi-intrinsic region when it has larger density than the deep levels. Increasing the doping density in general decreases the magnitude of the extrinsic radiative excess carrier lifetime. As the depth of the acceptor level increases, the magnitude of the extrinsic radiative excess carrier lifetime in general increases slightly due to the increase in the carriers freeze-out. Shallow acceptors are less sensitive to the low injection level illuminations as compared to the deep acceptor levels. The photo-responses of semiconductors with deep acceptors are very sensitive at very low temperature regimes. This is why most of the semiconductor photo detectors are working only at very low temperature regions.

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