STUDIES ON THERMOLUMINESCENCE PEAK INTENSITIES OF GERMANIUM QUANTUM DOTS

By

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A PROJECT SUBMITTED TO GRADUATE PROGRAMS IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE
AT
ADDIS ABABA UNIVERSITY
ADDIS ABABA
AUGUST 2020

ADDIS ABABA UNIVERSITY
DEPARTMENT OF
PHYSICS

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ADDIS ABABA UNIVERSITY

Date: **August 2020**

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Title: **Studies on Thermoluminescence Peak Intensities of Germanium Quantum Dots**

Department: **Physics**

Degree: **M.Sc.** Convocation: **August** Year: **2020**

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Abstract

In this project work I studied the TL properties of germanium Quantum dots in the one trap one recombination model for fist order kinetics. I simulated the TL glow curve for different parameters like the activation energy, the frequency factor, the heating rate and the initial concentration of the electrons in the conduction bands. The result shows that as the activation energy E is increased, the TL glow curve shifts towards higher temperatures, but the curve maintains its overall shape. Moreover, the initial concentration of filled traps has no effects on both the maximum height of the TL glow curve and the temperature of maximum TL intensity T_{max}, but leaves the overall shape unchanged in the case of the Garlick-Gibson model and May-Partridge model. I also showed that as the frequency factor s is increased, the TL glow curve shifts towards lower temperatures, but the curve maintains its overall shape for the three models. At the same time the effect of initial concentration of filled traps studied and showed that the initial concentration has no effects on the maximum height of the TL glow curve, and leaves the shape of TL glow curve unchanged.

Acknowledgements

- First and for most I would like to thank the almighty God for his help.
- I wish to express my sincere gratitude to my advisor Dr.Teshome Senbeta for his encouragement and support. Without his help, patience and useful supervision, it could be more challenging for me to complete this project.
- I am also very thankful to my beloved friends Waqgari Solomon my Father Eshetu Gemechu and brother Brhanu Eshetu for their support and encouragement.
- Finally I also appreciate Addis Ababa university instructors and ministry of education for financial support.

Alemayehu Eshetu
August, 2020

Chapter 1

Introduction

1.1 Statement of the Problem

The absorption of radiation increases the level of TL observed from a specimen by filling the localized energy levels with trapped electrons. But the heat absorbed from the surrounding reduces the number of trapped electrons by detrapping process. Thus, the intensity of the TL is a competition between trap filling by radiation and trap emptying by thermal excitation. At a given temperature of irradiation, many materials display an intensity of TL which is proportional to the amount of radiation absorbed, and this leads to the fact that TL may be used as a means of radiation dosimetry. The TL properties of the materials depend on the solid state properties of the material. TL can be used for different application and this applications motivate me to study the TL properties of germanium (Ge). I use theoretical and simulation methods to study the TL glow curves.

1.2 Objectives of the Study

The objective of this project is to discuss about types of thermoluminescent and study the effect of retraping of germanium quantum dots on TL intensity peaks corresponding to each trap like one recombination center model, kinetic orders using

different parameters such as, initial concentrations , frequency factor compare it with other factor. As a method of study, I employe analytical and numerical solutions of the electron rate equations governing the TL phenomena. Analytical solution of the rate equations are achieved by assuming negligible retrapping, whereas, the consideration of retrapping complicates the rate equations and hence numerical approaches are employed.

1.3 Thermoluminescence

Thermoluminescence is the emission of light from insulator or semiconductor when it is heated [1]. Thermoluminescence finds favor in diverse scientific disciplines as archaeology, geology, medicine, solid-state physics, biology and organic chemistry. Thermoluminescence (TL) should not be confused with the light spontaneously emitted from a substance when it is heated to incandescence. At higher temperatures a solid emits (infra) red radiation of which the intensity increases with increasing temperature that was referred as thermal or black body radiation. TL, however, is the thermally stimulated emission of light following the previous absorption of energy from radiation.

To describe TL, three essential ingredients are necessary. Firstly, the material must be an insulator or a semiconductor, metals do not exhibit luminescent properties. Secondly, the material must have at some time absorbed energy during exposure to incising radiation. Thirdly, the luminescence emission is triggered by heating the material [1]. A thermoluminescence material is thus a material that during exposure to ionizing radiation absorbs some energy, which is stored. The stored energy is released in the form of visible light when the material is heated. Note that TL does not refer to thermal excitation, but to stimulation of luminescence in a sample which was excited in a different way. This means that a TL material cannot emit light again by simply cooling the sample and reheating it another time. It should

first be re exposed to ionizing radiation before it produces light again. There are different sources of excitation, namely, ultraviolet (UV) light, X-rays, gamma-rays, etc. For instance, some minerals show some kind of luminescence under ultra violet light exposure and some need X-ray bombardment. Luminescence phenomena can also be observed in organic solids. While the luminescence of inorganic solids is mostly due to impurity atoms or other lattice defects, the luminescence in organic solids is attributed to molecular complexes. After the absorption of radiation, the emission of light takes place in a characteristic time t and this parameter allows us to sub-classify the process of luminescence. Conventionally emissions with decay time shorter than $10^{-8}s$ are referred as fluorescence and those with decay time greater than that are known as phosphorescence and this phenomenon is shown in Fig.1.1

While fluorescence takes place simultaneously with the absorption of radiation and stops immediately when the radiation ceases, phosphorescence continues to be observed after the excitation has been removed. In other words, phosphorescence takes place under the involvement of some meta stable state M, which is an energy level from which transitions to any lower energy levels are forbidden [1]. Thus, the luminescence that occurs after an electron is brought to a meta stable state as a result of the excitation of the system is called phosphorescence.

If a system brought to its meta stable state is completely unperturbed, then it would remain in such a state for a relatively long period. Absorption transition from the ground state (G) to M is also forbidden, though it can be reached indirectly as shown in Fig.1.2. For example, after an electron has attained the state E as a result of excitation shown by *(transition 1)*, it can fall to M *(transition 3)*. Consider the conditions that M is separated from E by a small energy gap and the system is in thermal equilibrium with its surrounding medium. Under such cases, the electron can return to state E following depopulation of the state M upon the application of some thermal energy. From there, transitions can take place as described in the case of

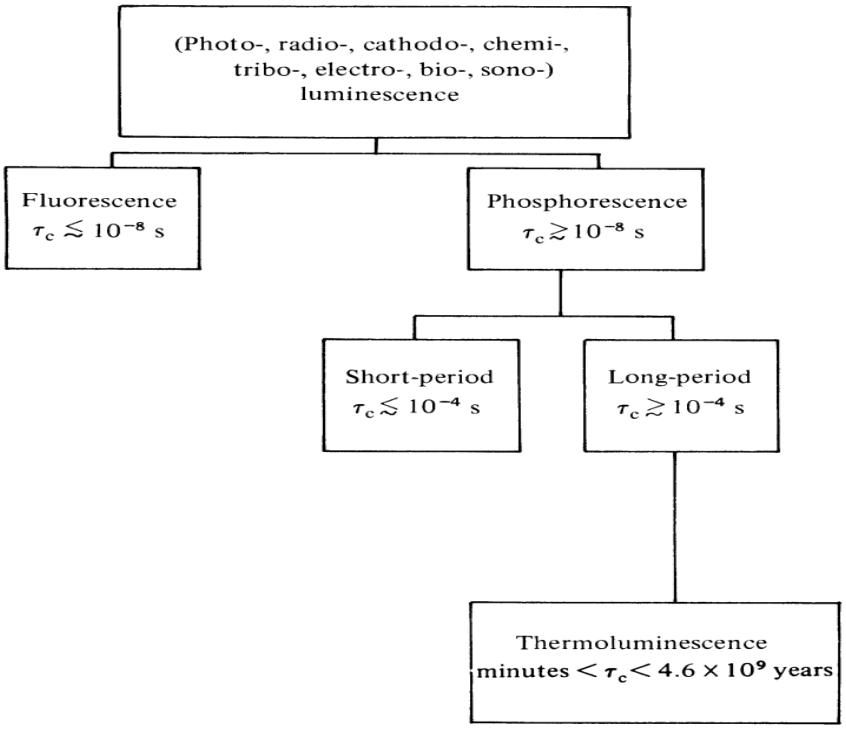

Figure 1.1: The types of luminescence based on the characteristic time t for the emission of light to take place [1].

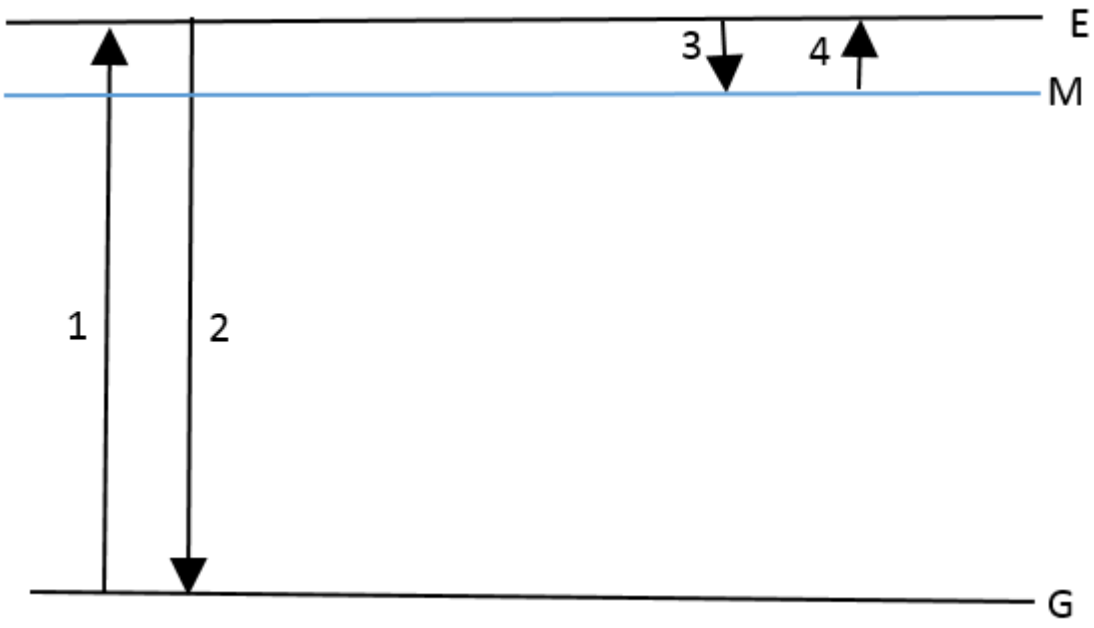

Figure 1.2: Energy level diagram illustrating (1) excitation, (2) emission, (3) falling to meta stable state, and (4) depopulation of the meta stable state. [1]

fluorescence *(transition 2)*. Therefore, phosphorescence spectrum contains emissions which are also present in fluorescence. Since the emission intensity changes with even small change in temperature, phosphorescence is sensitive to changes in temperature in contrast to fluorescence. A phosphor emits energy from an excited electron as light and the excitation of the electron is triggered by absorption of energy from one of the external excitation sources discussed above. An excited electron occupies a quantum state whose energy is above the minimum energy ground state.

In general, luminescence emission is explained by the transfer of energy from radiation to the electrons of the solid, thus exciting the electrons from a ground state to an excited state. The emission of a luminescent photon takes place when an excited electron returns to a lower energy state. An electron excited to an upper energy level can return to the ground state by re-emitting a photon of the same energy as was absorbed. This phenomenon is called resonance fluorescence.

Depending on the presence of other meta stable states relative to the excited state energy level, emission of photon of lower energy *(Stoke's shift)* or higher energy *(anti-Stoke's shift)* as compared to the absorbed energy can be observed when an excited electron relaxes to the ground state [1]. The wavelength of the emitted light is characteristic of the luminescent substance and not of the incident radiation. Usually, most studies of luminescence phenomena are concerned with the emission of visible light, but other wavelengths can be emitted, such as ultra-violet or infra-red.

A phosphor, most generally, is a substance that exihibits the phenomenon of luminescence. This includes phosphorescent materials, which show a slow decay in brightness(greater than 1 ms) and fluorescent materials, where the emission decay takes place over tens of nanoseconds. Phosphorescent materials are known for their use in radar screens and glow in the dark materials, whereas fluorescent materials are common in cathode ray tube (CRT) and plasma video display screens, fluorescent lights, sensors, and white LEDS. Phosphors, are often transition-metal compounds of

various types. The most common uses of phosphors are in CRT displays and fluorescent lights. Let us consider an energy band scheme having three localized levels as shown in Fig. 1.3. The two levels act as traps (TR1 and TR2) and the other acts as recombination center (R). The absorption of radiation of energy greater than the band gap energy results in the ionization of valence electrons, producing free electrons in the conduction band and free holes in the valence band respectively (transition 1). The electrons and holes may either recombine with each other or become trapped at the trap centers. In order for recombination to occur holes first become trapped at centers (R) (transition 7). Recombination takes place via the annihilation of the trapped holes by free electrons (transition 6). If the recombination transition is assumed to be radiative, then luminescence will result. The free electrons may also become trapped at levels TR1 and TR2 (transitions 2 and 4) in which case recombination can only take place if the trapped electrons absorb enough energy E1 and E2, respectively, to be released back to conduction band (transitions 3 and 5), from where recombination is possible. In other words, the TL occurs when the trapped electrons absorb enough energy in the form of heat to be released back to the conduction band from where there is possible recombination of electrons and holes. The energy required for the trapped electrons to be released back to the conduction band is called the trap depth (activation energy).

1.4 Applications of Thermoluminescence

1.4.1 Radiation dosimetry

The increased use of thermoluminescence which became evident in the late 1940s and early 1950s was only partly due to the work of Randall and Wilkins and of Garlick and Gibson. The absorption of radiation increases the level of thermoluminescence observed from a specimen by filling the localized energy levels with trapped electrons.

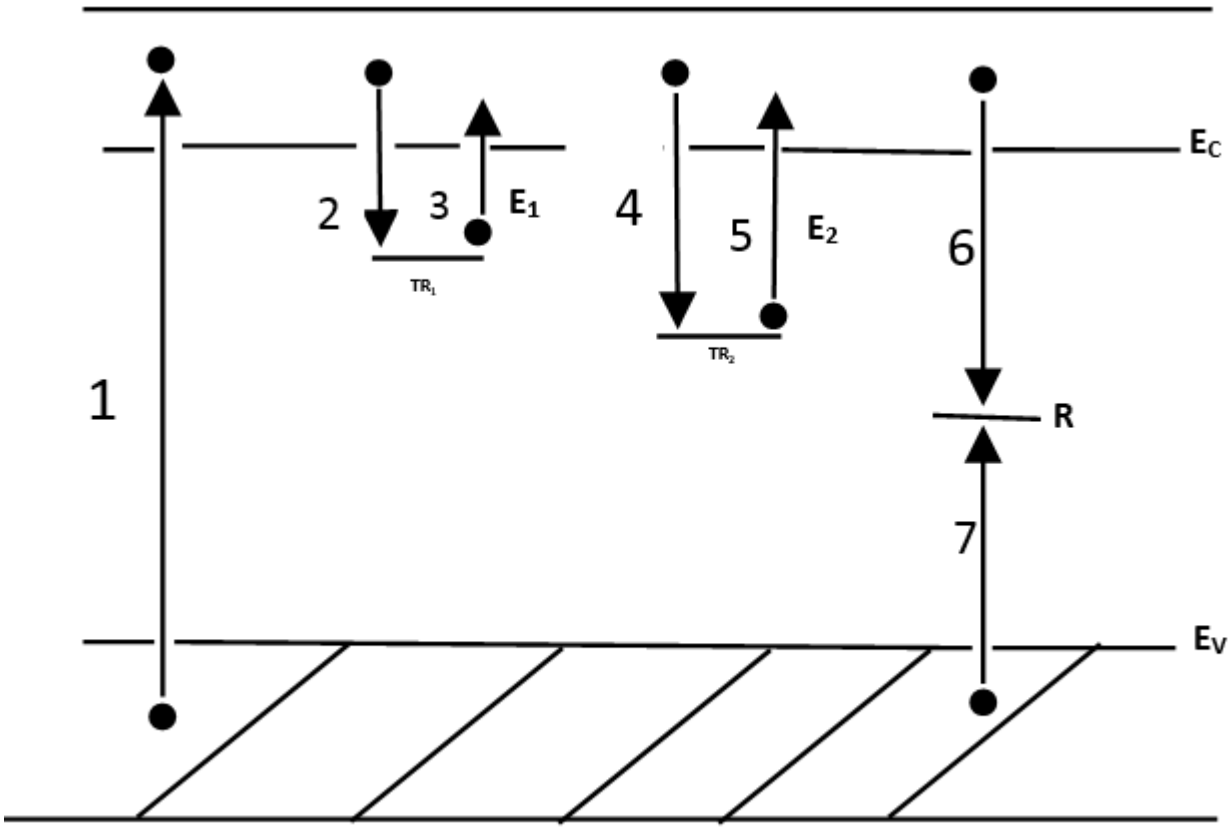

Figure 1.3: Three level model for thermoluminescence where E_V is energy in the balance band and E_C is energy in the conduction band . Allowed transitions: (1) ionization; (2), (4) and (7) trapping; (3) and (5) thermal release; (6) radiative recombination and emission of light [1].

The absorption of heat from the environment, on the other hand,tends to reduce the numbers of trapped electrons by thermally releasing them. At a given temperature of irradiation, many materials display an intensity of thermoluminescence which is proportional (or nearly so) to the amount of radiation absorbed, and this led Daniels and colleagues[1] to propose that thermoluminescence may be used as a means of radiation dosimetry. The first proper application of thermoluminescence to dosimetry was in 1953 when LiF(lithium fluoride) was used to measure radiation following an atomic weapon test . LiF(lithium fluoride) did not re- emerge as a first class dosimetry until the work of Cameron and his colleagues. It had been known since the work of Wiedemann and Schmidt that the presence of impurities within a crystal enhances the thermoluminescence response and so it was that the sensitivity of LiF(lithium fluoride) was found to be improved by the incorporation of impurities.

1.4.2 Age determination

Once the relationship between thermoluminescence intensity and absorbed radiation dose had been established it was only a short step to the use of thermoluminescence as a means of age determination. This application of thermoluminescence was also first suggested by Daniels and colleagues who offered the premise that the natural thermoluminescence from rocks is directly related to the radioactivity from uranium, thorium and potassium present within the material. This radioactivity results in the accumulation of a so called *'geological'* dose [1]. If the rate of irradiation from the radioactive minerals is established, and if the rate of thermal release of the thermoluminescence during the rock's irradiation can be shown to be negligible, then the length of time over which the rock has been irradiated can be determined from:

$$age = \frac{absorbed \;\; dose}{dose \;\; rate} \tag{1.4.1}$$

1.4.3 Geology

Age determination is not the only way that thermoluminescence is utilized in geology. In some instances thermoluminescence is more sensitive for detecting traces of radioactivity than more conventional means - e.g., a Geiger counter or a scintillation.

1.4.4 Defects in solids

Defect concentrations, enthalpies and energies of formation and activation and other relevant parameters are generally determined from studies of ion movement, such as ionic conductivity, diffusion, defect reactions, etc. This type of measurement has been supplemented by many other techniques including optical absorption, electron spin resonance, X-ray diffraction, photoconductivity, optical scattering, impurity decoration and many more, all of which can serve for comparison with the other 'dynamic' methods.

In principle, it has been known that thermoluminescence is particularly sensitive to traces of impurities within the specimen. It is believed that the impurities give rise to the localized energy levels within the forbidden energy gap. TL is very sensitive to traces of impurities or defects within the host material of a given sample and experiments on TL yields useful information on the properties of the various types of defect present within an insulator or semiconductor. This includes the position of the defect within the energy gap and sometimes the type of defect itself. In general the impurities give rise to the localized energy levels within the forbidden energy gap and that these are crucial to the TL process [1]. Other applications in recent years thermoluminescence from DNA base analogues has been observed. These materials act as tumour inhibitors by a mechanism of radical conversion and it is hoped that thermoluminescence will help us to understand the charge transfer processes involved [1]. The technique has also been used to identify the dust particles responsible for lung disease in miners and the volcanic soil responsible for non filarial elephantiasis.

Chapter 2

Types of Thermoluminescence and its Characteristics

2.1 Types of thermoluminescence

According to the type of radiation used to excite the emission, luminescence can be classified in to different types. These are photoluminescence, electroluminescence, optically simulated luminescence, thermoluminescence, cathodoluminescence, chemiluminescence, bioluminescence, triboluminescence, radioluminescence (scintillation), ionoluminescence, etc.

2.1.1 Optically stimulated luminescence

Optically stimulated luminescence (OSL) is a method for measuring doses from ionizing radiation. It is used in at least two applications: luminescence dating of ancient materials: mainly geological sediments and sometimes fired pottery, bricks etc., although in the latter case thermoluminescence dating is used more often radiation dosimetry, which is the measurement accumulated radiation dose in the tissues of health care, nuclear, research and other workers, as well as in building materials in regions of nuclear disaster. The trapping sites are imperfections of the lattice impurities or defects. The ionizing radiation produces electron-hole pairs: Electrons are

in the conduction band and holes in the valence band.

The electrons that have been excited to the conduction band may become entrapped in the electron or hole traps. Under stimulation of light the electrons may free themselves from the trap and get into the conduction band. From the conduction band they may recombine with holes trapped in hole traps. If the center with the hole is a luminescence center (radiative recombination center) emission of light will occur. The photons are detected using a photomultiplier tube. The signal from the tube is then used to calculate the dose that the material had absorbed [2].

2.1.2 Photoluminescence

Photoluminescence occurs after excitation with light (i.e., radiation within the optical range). This excitation with electromagnetic radiation imparts external energy on an electron in a semiconductor or insulator and makes it excited to a higher energy quantum state. If the electron returns (relaxes) to a lower energy quantum state by radiating a photon, the process is called photoluminescence (PL) [3]. This can be described as an excitation to a higher energy state and then a return to a lower energy state accompanied by the emission of photon. In PL phenomena, the period between absorption and emission is of the order of 10nanoseconds, which is extremely short. The PL intensity depends on the measurement of temperature and the energy of the exciting light. The PL emission can be divided in to fluorescence and phosphorescence as discussed above.

2.1.3 Electroluminescence

When a material emits electromagnetic radiation as a result of the application of an electric field, the process is called electroluminescence (EL). [4] The photon emitted results from radiative recombination of electrons and holes created in the phosphor by the voltage between the two electrodes. One of the electrodes is transparent to the

wavelength of the light emitted by the device. In other words, electroluminescence is the efficient generation of light in a non-metallic solid or gas by an applied electric field or plasma. Another type of electroluminescence is that produced by some crystals when an electric current passes through them. In this case the current or electrons excites electrons that occupy energy levels involved with chemical bonds inside the crystal. When the excited electrons decay back to their ground state, they emit visible light. Both organic and inorganic light emitting diodes (LEDs), operating on a different principle, has now become a widely used application of electroluminescence [5].

2.1.4 Thermoluminescence

Thermoluminescence (TL), which is also called radiation induced thermally stimulated luminescence or simply thermally stimulated luminescence (TSL), is the thermally stimulated emission of light following the previous absorption of energy from radiation. The primary causes for the induction of TL in a given material are the ionization radiations such as (χ-rays, γ-rays, UV light, etc,) to which the sample is pre-exposed. However, the application of heat stimulates the release of the stored energy in the sample due to pre-exposure to the ionizing radiations which in turn produces luminescence. Therefore, heat has only a secondary role in the process of TL. The particular characteristic of a TL material is that, once heated to excite the light emission, the material can not be made to emit TL again by simply cooling the specimen and re-heating [6]. For the luminescence emission to occur again, the material should be re-exposed to one of the ionizing radiations, where upon heating the sample once again produces light emission.

2.1.5 Cathodoluminescence

Cathodoluminescence (CL) is the characteristic visible radiation (color) occurring due to bombardment by electrons (cathode rays) [7]. Luminescence in CL is typically more intense than that produced by ultraviolet light and is also observed in minerals that do not luminesce under ultraviolet light. It is a very useful form of luminescence since beams of electrons are used for many purposes. For example, the electron microscope employs beams of electrons to produce high resolution images of small specimens and in some cases, the beam produces CL from the specimen. This is important for the study of minerals in rocks where the presence of transition metal trace elements can cause the mineral to give off a distinctive color light [8].

2.1.6 Chemiluminescence

Chemiluminescence is produced as a result of a chemical reaction usually involving an oxidation reduction process [9]. The most common mechanism for such an emission is the conservation of chemical energy, released in a highly exothermic reaction, into light energy in the visible region. In some chemical reactions energy can be transferred to electrons in the chemical bonds. As these electrons decay down to lower excited states, they emit light. Some of these reactions proceed slowly, so the light can be emitted for a considerable time. This is known as chemiluminescence. This is distinct from more vigorous chemical reactions where so much heat is released that the chemicals actually catch fire or otherwise glow red hot (incandescence). However the process of chemiluminescence remains to be not fully understood. Lyoluminescence, which is the phenomenon of light emission during the dissolution of previously irradiated solids in suitable solvents is a type of chemiluminescence [10] .

2.1.7 Bioluminescence

Electronic excited states of the bio molecules can be produced due to biochemical reactions inside the cells of the living organisms such as fire flies, glow-worms, some bacteria, fungi and many sea creatures (such as planktons) both near surface and at great depths and interesting luminescence phenomena can be observed from these living beings [11]. The chemical reactions are the enzymic oxidations. For example, the oxidation of luciferin in the presence of enzyme luciferase is responsible for occurrence of bioluminescence.

2.1.8 Triboluminescence

Triboluminescence is the emission of light on applying an external mechanical energy inducing stress. It could be excited by cutting, cleaving, grinding, rubbing, and compressing or by impulsive deformation of solids. Because of this it can also be called mechanoluminescence. B. V. Bukvetskii et al, described the phenomenon of triboluminescence as the glow resulting from crystal destruction or friction [12] and stated its importance in the process of converting mechanical energy into light energy. It has been observed that all piezoelectric crystals exhibit triboluminescence and it is sometimes called piezoluminescence.

2.1.9 Radioluminescence(Scintillation)

Radioluminescence is produced by ionizing radiation [13]. Some polymers contain organic molecules which emit visible light when exposed to such radiations as X-ray, γ-rays, or cosmic rays. It is also called scintillation because it is used as a technique to detect individual light pulses generated by the incidence of each X-ray photon or a nuclear particle [14]. Such light pulses are called scintillations, since like a spark they are very short-lived. The intensity of the scintillation (light pulse) is directly proportional to the incident γ-ray photon energy when it is totally absorbed. The

measurement of the pulse intensity, therefore, provides the means for knowing the γ-ray energy. The mechanism of light emission in radioluminescence and cathodoluminscence is same because in both the cases it is the electrons, incident primarily from cathode rays or the secondary electrons produced after the first interaction of the incident X-ray photon or nuclear particle, which cause the excitation of the luminescent species in the bulk sample.

2.1.10 Ionoluminescence

Another interesting method of producing luminescence is the visible light produced when fast ions collide with organic and inorganic compounds. This is called ionoluminescence and it can also be defined as a phenomenon of non-thermal light emission induced by high energy accelerated particles or ion beams [15]. An early application of ionoluminescence was to luminous clock dials. These relied upon a rather hazardous method of making light that involved radioactivity. A radioactive material, such as radium, was mixed with a material that displays luminescence, such as zinc sulphide. As the radium decays, it emits alpha particles and other radiation. This excites electrons in the luminescent material to give off light. This is very handy, since the light persists indefinitely, limited only by the half life of the radium isotope used, ^{226}Ra, which is 1600 years.

2.2 Characteristic of luminescence

Characteristic of luminescence occurs by doping the host lattice with either transition (3d) or rare-earth (4f) metal ions (impurities) that substitute for host lattice cations [16]. An electron gets excited to a higher energy level in the atom itself. Rare earth ions from Ce^{3+} (atomic number of 58) to Yb^{3+}(70) have partially filled 4f orbital with energy levels characteristic to each ion and show a variety of luminescent properties around the visible region. Many of these ions can be used as luminescent ions in

phosphors. There are 15 rare earth materials and the lanthanides are those rare earths with the atomic numbers between 57(La) and 71(Lu). The 4f electronic energy levels of lanthanide ions are characteristic of each ion. The levels are not affected much by the environment because 4f electrons are shielded from external electric fields by the outer $5s^2$ and $5p^6$ electrons. This is in strong contrast with transition metal ions, whose 3d electrons, located in an outer orbit, are heavily affected by the environmental or crystal electric field [16]. Typical phosphor used in cathode ray tube (CRTs) and Field emission displays (FEDs) consist of a host matrix doped with activators such as the rare earths (4f) and the transition metals(3d). [17]

2.3 Defect centers and mechanism of thermoluminescence

Irradiation of a sample causes transitions of electrons between the valence band and the conduction and creating free electrons in the conduction band and free holes in the valence band. Though some electrons and holes undergo recombination almost instantaneously during irradiation, some still diffuse in the lattice[1] and remain trapped in the defect center. These imperfections in the crystal, associated with impurities and or lattice defects may create new localized energy levels in the forbidden band gap whose positions depend on the nature of the imperfections defects and the host lattice.

This means that TL is very sensitive to the presence of defects or impurities in a given sample. There is also another type of defect which is associated with impurities, for example, ions of transition elements. This is usually the main cause of a characteristic color from certain minerals. The color is due to absorption bands caused by electronic transitions between energy levels in the band gap. The wave functions of the transition ions (in particular 4f ions) are highly localized [20]. As mentioned above, the energy levels in the band gap depend on the nature of the imperfection, lattice defect

or impurity and can in principle be located at any energy position varying from just below the bottom of the conduction band to just above the top of the valence band. A variety of defects which are associated with energy levels in the forbidden band gap are also produced during exposure to ionizing radiation.

As the concentration of radiation-induced defects is small, the number of defects usually increases with increasing radiation dose. Ultimately, for very high doses, one might expect that the concentration of the radiation induced defects saturates. That is with increasing dose the concentration of radiation-induced defects reaches a maximum value. Due to their long term exposure to ionizing radiation extremely old minerals are often metameric, which means that the long-range order is absent and the structural properties of these minerals are similar to those of amorphous materials like glasses. These heavily damaged minerals are not suited for TL dating purposes. As a result of the structural changes during the long-term exposure, the physical properties, in particular the TL controlling properties have changed drastically. Due to their high mobility, free electrons and holes produced by ionizing radiation can migrate in the crystal until they are trapped by different trap centers such as impurities, luminescent centers and other imperfections in the crystal. A trap is characterized by the energy **E** that a trapped electron(or hole) must acquire from lattice vibrations to escape to the conduction band(or valence band).

A necessary condition for a mineral to be a suitable luminescent material for TL dating is that the relevant traps are deep, i.e., not easily emptied. This implies that the energy of the trapped electron should be located sufficiently far from the bottom of the conduction band. Similarly, the energy of the trapped hole should be located sufficiently far from the top of the valence band. In TL, during the heating stage, different kinds of transitions of electrons and holes can take place during the detrapping process from their respective trap centers so that luminescence can occur.

Chapter 3

Optical and Thermoluminescence Properties of Germanium and Its Potential Applications

3.1 Optical properties of Germanium

There may be a direct or indirect band gap existing in semiconductors. The semiconductors with direct band gap are able to emit a photon when excitation is done by the wavelength required. On the basis of this property, the development of applications like LEDs, lasers etc came in action [18]. The semiconductors with indirect band gap can be made of the type direct band gap by simply alloying. Germanium is an indirect band gap semiconductor and it has a face centered cubic crystal lattice structure of diamond type with a lattice constant of $a = 5.657$. Germanium is a typical semiconductor, carrying a specific resistance of 500Ω at room temperature, making germanium an indirect band gap semiconductor, suitable for light emitting devices. Ge is one of the $group - IV$ semiconductors, having an indirect band structure similar to Si. The related indirect electron transitions are with higher probability responsible for absorbtion and emission of light. For this case, the width of the energy gap is given by 0.6 eV $\leq E_{gi} \leq$ 0.8 eV. It can be observed another bottom of the conduction band which is directly above the maximum of the balance band and the

related direct energy gap is given by $E_{gd} \geq 0.8$ eV [19]. The width of the band gap becomes smaller with increasing temperature. Due to the thermal expansion, the lattice constant changes which cause a change in the band structure which is small. Therefore, in germanium, light absorption can occur in the begging at energy of 0.6 eV due to indirect transition and at 0.8 eV due to direct transitions. The value of the extinction coefficient for germanium is given by around $10^2 cm^{-1}$ in the first region, $10^{-4} cm^{-1}$ in the second region, and increasing up to $10^6 cm^{-1}$,if the photon energy becomes larger than 3.0 eV [19]. Germanium films deposited at the room temperature are in the amorphous phase. In principle germanium begins to crystallize at higher temperature, which occur above a substrate temperature of T_s [20]. This municipality of properties makes such films suitable for broad usage in manufacturing a number of electronic devices such as light detectors, hetrojunctions, and sensors for temperature and magnetic field. From the viewpoint of photonic devices, Ge is often regarded as quasi-direct band gap material, since the difference of conduction band energy between the indirect L valley and the direct Γ valley is as small as 0.14 eV. It is important that the direct band gap energy of 0.80 eV corresponds to 1.55 μm in wavelength. As a result, Ge shows a large optical absorption below 1.55 μm, being suitable to photodiodes (PDs) in the optical communication band. Although Ge possesses a large lattice mismatch of 4% with Si, high-quality Ge epitaxial layers can be grown using chemical vapor deposition (CVD)techniques with a low$\sim$high temperature two-step growth. It has been shown that when germanium is subjected to a tensile strain and a heavy n-doping level, at room-temperature photoluminescence(PL) can be greatly enhanced [21]. Among these two factors, achieving a heavy n-doping level in Ge (i.e., electron concentrations higher than $1 \times 10^{19} cm^{-3}$) is a challenge since the solubility of most $group - V$ elements(P, As, Sb) in Ge is very low. An active phosphorus concentration up to $2 \times 10^{19} cm^{-3}$ and room temperature PL measurements reveal an intensity enhancement up to 50 times. This result opens a

new route for the realization of optoelectronic devices [22]. Optical properties such as absorption and extinction coefficients greatly influence the behavior of Ge semiconducting material, which determines the amount of light absorbed by the materials, most especially in the infrared region of the spectrum [23].

3.2 Thermoluminescence Properties of Germanium

The study on TL intensity and corresponding standard deviation of Al_2O_3 at different Ge concentration showed that two peaks, one prominent peak at around $175C^o$ and another hump around $230C^o$. The TL intensity of the TL peak arrive the maximum value at 0.3% mol [29].The figure indicates the TL intensity increase as the delivered dose increase.

A research group reported the characteristics of the thermoluminescence (TL) response of Ge-doped optical fibers with various energies and exposures of photon irradiation [24]. The Ge-doped fiber and Thermoluminescence Dosimeter (100)(TLD100) show linear response as a function of current and time using X-ray photon of energy 60 kV , 80 kV and 100 kV. When irradiated with 60 kV, 80 kV and 100 kV X-ray energy at various currents (mA), tube distance (cm) and exposure time (second) ranges, TLD100 media provide a TL yield up to two times that of Ge-doped fibers. The energy response of the Ge-doped fibers is linear and similar over the 60 kV $\sim$100 kV energy range, and its sensitivity is 0.39 $\pm$ 0.05 of the TLD100 media.

The comparative analysis of radiation measurements for Ge-doped fibres of differing dopant concentrations and dimensions(in essence studying the effect of the fraction of fibres occupied by the dopant)and Ge dopant concentration were reported by [25]. The intension of the study was to develop new TL dosimeters of optimum performance for radiotherapy applications [26]. The result shows notable, for both the larger cylindrical and smaller dimension fibres, is the good linear response for photon irradiations from 0.5 Gy up to 10 Gy, the greatest TL signal being obtained for the

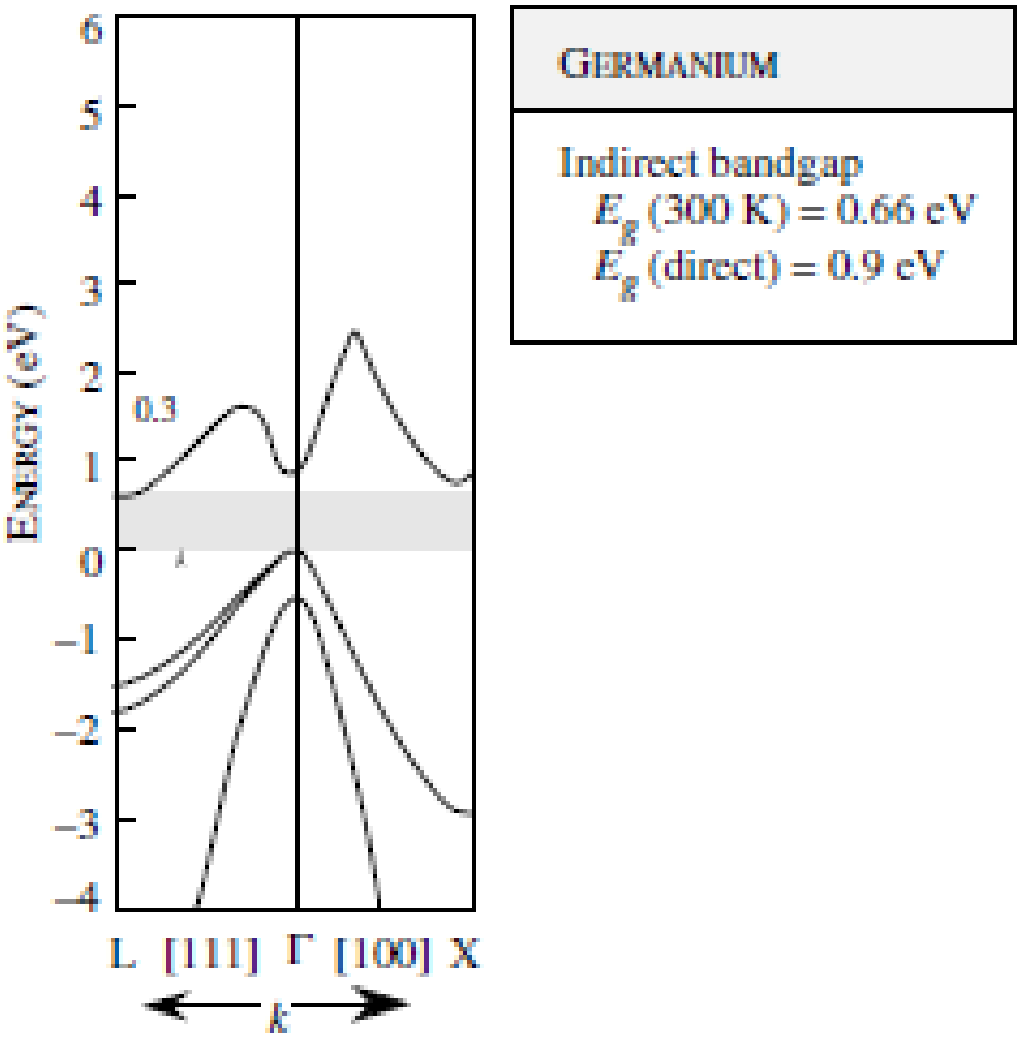

Figure 3.1: Band structure of Germanium[23]

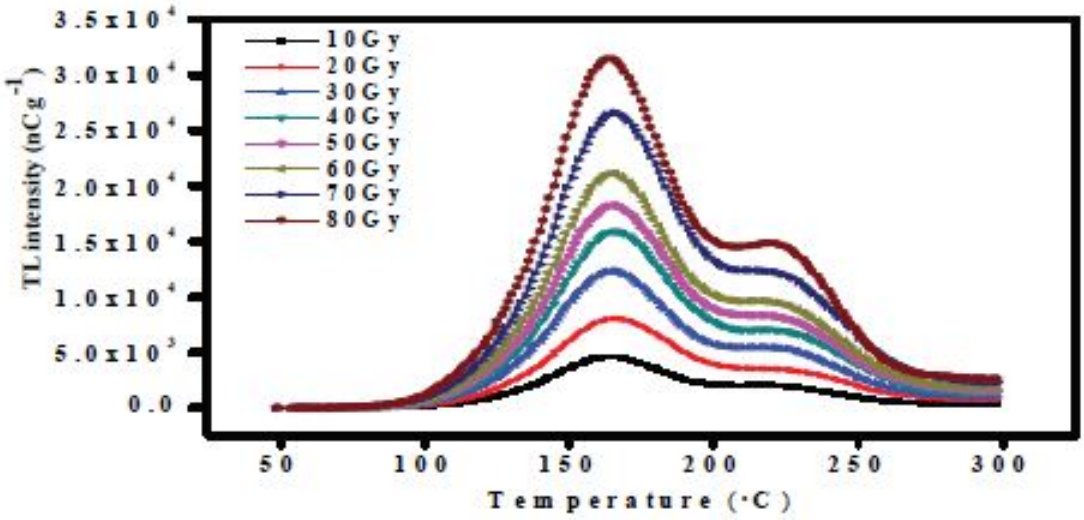

Figure 3.2: TL glow curve of 3.0 mol% germanium doped aluminium oxide at different doses of Cobalt-60 gamma rays [29].

6 mol %Ge doped optical fibres. These investigations were provided valuable information in obtaining a more detailed understanding of the development of novel Ge doped optical fibres for dosimetry in the radiotherapy energy range.

The characterisation of new fabricated material Ge doped silica glass thermoluminescence dosimeter for medical radiation dosimetry at therapy energy was studied [26]. The finding shows 120 m fibres have 1.82 greater dose response than 604 pm fibres irradiated at 6 MeV photon with a fixed dose of 3 Gy. While for electron energy 12 MeV, the response shows 120 m fibres have 1.58 greater dose response compared to 604 m fibres. The good responses are suitable to make these tailor-made doped silica fibres a promising TL material for use as a dosimetric system in medical radiation therapy.

Similar studies carried out on germanium doped calcium borate glasses to investigate thermoluminescence properties to seek their possibility to use as glass radiation dosimeter [27]. The results indicate that this glass has a potential to be used as a radiation dosimetry, especially for application in radiotherapy.

3.3 Application of germanium

The major end uses for germanium in 2007, worldwide, were estimated to be: 35% for fiber-optics, 30% infrared optics, 15% polymerization catalysts, and 15% electronics and solar electric applications. The remaining 5% went into such uses as phosphors, metallurgy, and chemotherapy.

3.3.1 Optics

The notable properties of germania (GeO_2) are its high index of refraction and its low optical dispersion. These make it especially useful for wide-angle camera lenses, microscopy, and the core part of optical fibers [28]. At the end of 2002, the fiber optics industry consumed 60% of the annual germanium used in the United States, but this

is less than 10% of worldwide consumption. It is used in infrared spectroscopes and other optical equipment that require extremely sensitive infrared detectors [29]. It has replaced titania as the dopant for silica fiber, eliminating the subsequent heat treatment that made the fibers brittle. Because germanium is transparent in the infrared wavelengths, it is an important infrared optical material that can be readily cut and polished into lenses and windows. It is especially used as the front optic in thermal imaging cameras working in the 8 to 14 micron range for passive thermal imaging and for hot-spot detection in military, mobile night vision, and fire fighting applications [30]. It has a very high refractive index (4.0) and must be coated with anti-reflection agents. Particularly, a very hard special antireflection coating of diamond-like carbon (DLC), refractive index 2.0, is a good match and produces a diamond-hard surface that can withstand much environmental abuse [31].

3.3.2 Electronics

Silicon-germanium alloys are rapidly becoming an important semiconductor material for high-speed integrated circuits. Circuits utilizing the properties of Si-Ge junctions can be much faster than those using silicon alone [32]. Silicon-germanium is beginning to replace gallium -arsenide (GaAs) in wireless communications devices. The Si-Ge chips, with high-speed properties, can be made with low-cost, well-established production techniques of the silicon chip industry. Solar panels are a major use of germanium. Germanium is the substrate of the wafers for high-efficiency multi-junction photovoltaic cells for space applications [33]. High-brightness LEDs, used for automobile headlights and to back light LCD screens, are an important application. Because germanium and gallium arsenide have very similar lattice constants, germanium substrates can be used to make gallium arsenide solar cells [34]. The Mars Exploration Rovers and several satellites use triple junction gallium arsenide on germanium cells.

3.3.3 Other uses

Semiconductors made of single crystal high-purity germanium can precisely identify radiation resources . For example in air port security [35], germanium is useful for monochromators for beam lines used in single crystal neutron scattering and synchrotron X-ray diffraction. The reflectivity has advantage over silicon in neutron and high energy X-ray applications [36]. Crystals of high purity germanium are used in detectors for gamma spectroscopy and the search for dark matter [37].

3.3.4 Germanium and health

Germanium is not considered essential to the health of plants or animals [38]. Germanium in the environment has little or no health impact. This is primarily because it usually occurs only as a trace element in ores and carbonaceous materials, and the various industrial and electronic applications involve very small quantities that are not likely to be ingested. For similar reasons, end-use germanium has little impact on the environment as a biohazard. Some reactive intermediate compounds of germanium are poisonous. There is no, however, no medical evidence suggests that such supplements are actively harmful. Some of $germanium^{'}s$ artificially produced compounds are quite reactive and present an immediate hazard to human health on exposure. For example Germanium chloride and germane (GeH_4) are a liquid, gas respectively. That can be very irritating to the eyes, skin, lungs, and throat [39]. Germanium supplements, made from both organic and inorganic germanium, have been marketed as an alternative medicine capable of treating leukemia and lung cancer [40]. In this chapter the optical and thermoluminescence properties of germanium and its potential applications models have been discussed in detail. In chapter-4, the discussion is about rate equations and thermoluminescence models.

Chapter 4

Rate Equation and Thermoluminescence Model

4.1 Rate equation

For three active electron traps with energy levels E_1, E_2 andE_3 below the bottom of the conduction band, the rate equations can be written as:[48]

$$\frac{dn_1}{dt} = -s_1 n_1 \exp\left(-E_1/kT\right) + n_c A_1 (N_1 - n_1) \tag{4.1.1}$$

$$\frac{dn_2}{dt} = -s_2 n_2 \exp\left(-E_2/kT\right) + n_c A_2 (N_2 - n_2) \tag{4.1.2}$$

$$\frac{dn_3}{dt} = -s_3 n_3 \exp\left(-E_3/kT\right) + n_c A_3 (N_3 - n_3) \tag{4.1.3}$$

$$\begin{aligned}\frac{dn_c}{dt} = s_1 n_1 \exp\left(-E_1/kT\right) + s_2 n_2 \exp\left(-E_2/kT\right) + s_3 n_3 \exp\left(-E_3/kT\right) - n_c A_1 (N_1 - n_1) \\ + A_2 (N_2 - n_2) + A_3 (N_3 - n_3) + (A_r n_h)\end{aligned} \tag{4.1.4}$$

Here $n_i (i = 1, 2, 3)$ (in cm^{-3}) is the concentration of trapped electrons on the levels E_i, $N_i (i = 1, 2, 3)$ is the total concentration of traps on the levels E_i, k is the Boltzmann

constant, s_i is the probability per unit time of an electron to escape from the i^{th} trap, A_i is the re-trapping probability on the i^{th} energy level (cm^3s^{-1}), n_c and n_h, respectively, are the concentration of the electrons in the conduction band and holes in the hole trap, and A_r is the electron-hole radiative recombination probability. The term s is commonly called the frequency factor, although when applied to thermoluminescence(TL) it is often called attempt-to-escape frequency. The usual interpretation of s is that it represents the number of times per second that a bound electron interacts with lattice phonos times transition probability. The maximum value expected for s is therefore the lattice vibration frequency, namely $10^{12} - 10^{14}s^{-1}$. The system (**4.1.1** to **4.1.4**) is closed by the quasi-neutrality condition.

$$n_1(t) + n_2(t) + n_3(t) + n_c(t) = n_h(t) \tag{4.1.5}$$

Here $n_h(t)$ is the instantaneous concentration of holes in hole trap. Basically the temperature of the system depends on time T=T(t). The generally acceptable is the linear heating rate where β is the heating rate.

$$T(t) = T_O + \beta t \tag{4.1.6}$$

4.2 First order kinetics(Randall and Wilkins Model)

In first order kinetics, the assumption is that there is a strong tendency to recombination and that electrons, which are released thermally from the traps and excited into the conduction band recombine quickly with trapped hole [41]. It assumes that the retrapping of electrons is negligible,for probability coefficients $A_i(i = 1; 2; 3)$. The probability p, per unit of time, that a trapped electron will escape from the trap, or the probability rate of escape per second, is given by the Arrhenius equation,

$$p = s.E \exp\left(-\frac{E}{kT}\right) \tag{4.2.1}$$

where E is the trap depth (eV), k the Boltzmannfs constant, T the absolute temperature (K), s the frequency factor (sec^{-1}), depending on the frequency of the number of hits of an electron in the trap, seen as a potential well. The life time, τ , of the charge carrier in the metastable state at temperature T , is given by

$$\tau = p^{-1} \tag{4.2.2}$$

If n is the number of trapped electrons in T , and if the temperature is kept constant, then n decreases with time t according to the following expression:

$$\frac{dn}{dt} = -pn \tag{4.2.3}$$

Integrating this equation

$$\int_{n_0}^{n} \frac{dn}{n} = -\int_{t_0}^{t} p.dt \tag{4.2.4}$$

one obtains

$$n = n_0 \exp[-\exp\left(\frac{E}{kT}\right).t] \tag{4.2.5}$$

This equation is the solution for first order kinetics, where n_0 is the number of trapped electrons at the initial time $t_0 = 0$. The TL intensity, I, at a costant temperature, is directly proportional to the detrapping rate, dn/dt :

$$I = -c\left(\frac{dn}{dt}\right) = cpn \tag{4.2.6}$$

where c is a constant which can be set to unity. Eq. 4.2.6 represents an exponential decay of phosphorescence. Using Eq. 4.2.5 in Eq. 4.2.6 one obtains:

$$I(t) = n_0 s \exp\left(-\frac{E}{kT}\right) \exp\left[-st\exp\left(-\frac{E}{kT}\right)\right] \tag{4.2.7}$$

Introducing a constant heating rate, $\beta = \frac{dT}{dt}$, from Eq.4.2.4 we have: $\int_{n_0}^{n} \frac{dn}{n} = -\left(\frac{s}{\beta}\right) \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) dT'$

$ln(n) - ln(n_0) = -\left(\frac{s}{\beta}\right) \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) dT'$ and again then, using Eq.4.2.6

$$n_i(T) = n_{i0} \exp\left(-\frac{s_i}{\beta}\right) \int_{T_0}^{T} \exp\left(-\frac{E_i}{kT}\right) dT \tag{4.2.8}$$

where $n_{i0}(i = 1, 2)$ are the initial concentration of electrons in the traps. It is generally accepted that the density number of electrons in the conduction band $n_c(t)$ is slowly varying function of time and practically is a constant on the typical times of the TL. Using rate of equation we obtain

$$\frac{dn_c}{dt} \approx 0 \tag{4.2.9}$$

Using Eqs. (4.1.3), (4.1.6), (4.2.8), and (4.2.9), we obtain the intensity of the TL from each trap in the first order kinetics.

$$I(T) = n_{i0} s_i \exp\left(-\frac{Ei}{kT}\right) \exp\left[\left(\frac{-s}{\beta}\right) \int_{To}^{T} \exp\left(-\frac{Ei}{kT}\right) dT\right]. \tag{4.2.10}$$

An important relationship, the so called condition at the maximum, is obtained by Eq.4.2.10 by setting its first derivative equal to zero at $T = T_M$, i.e, $\frac{dI}{dT} = 0$ at $T = T_M$ For practical purposes, the logarithm derivative is considered: $\frac{d(lnI)}{dT} = \frac{1}{T}\frac{dI}{dT}$ then from Eq.4.2.10 one obtains
$\left[\frac{d(lnI)}{dT}\right]_{T=Tm} = \frac{E}{kT_M^2} - \frac{s}{\beta} \exp\left(\frac{-E}{kT_M}\right) = 0$ and the following expression is obtained

$$\frac{\beta E}{kT_M^2} = s \exp\left(\frac{-E}{kTM}\right) \tag{4.2.11}$$

4.3 Second order and a case beyond second order kinetics(Garlick and Gibson Model)

Garlick and Gibson (GG) [42] modified the model of Randall wilkins (RW) for the TL intensity using the same one trap one recombination center (OTOR) model. They assume that once an electron is thrown out from the trap into the conduction band, it may either recombine with a RC to produce luminescence or it may be retrapped

by any of the vacant traps. This is in contrast to the (RW) model in which retrapping is ignored. If we assume that the probability coefficients for recombination and retrapping are A_h and A_n respectively, the probabilities for any excited carrier for recombination and retrapping would respectively be $A_h n$ and $A_n(N-n)$, where N is the total number of the traps and n is the number of available RC at any time. In the one trap one recombination model(OTOR), n is also equal to the number of filled traps, so that the charge balance is maintained. The combined probability of both the transitions thus is $A_h n + A_n(N-n)$. The recombining fraction F of this combined probability of transitions for any excited carrier, then is

$$F = \frac{A_n n}{A_n n + A_n(N-n)}, \tag{4.3.1}$$

$$I(T) = \frac{-dn}{dt} = (\frac{n}{N}) n s \exp(-E/kT) = \left(\frac{n^2}{N}\right) s \exp(-E/kT). \tag{4.3.2}$$

The intensity I being proportional to n^2, the TL in this model is called by the name as TL of second order (SO) kinetics. Assuming as usual $dt = \frac{dT}{\beta}$, integration of (4.3.2) yields the value of n at any temperature T. Multiplying the value of n by the escape probability $p(= s \exp(-E/kT))$, gives the equation for glow curve.

$$I(T) = {n_0}^2 \left(\frac{s}{N}\right) \exp\left(-E/kT\right) \left[1 + \frac{n_0}{s}\beta N \int_{T_0}^{T} \exp\left(-E/kT\right) dT'\right]^{-2} \tag{4.3.3}$$

It is worth while to mention here that second order(SO) kinetics is obtained in one trap one recombination center (OTOR) model even if $A_h = A_n$. The concentration h of recombination center (RC), is equal to the concentration n of the filled active traps ($h = n$),(so that the overall charge neutrality is maintained),it becomes a case of SO kinetics. Because under the condition $A_h \neq A_n$, the reaction rate between the realsed charge from the traps and the RC becomes equal to n^2 which means kinetic order equal to 2. For $A_h = A_n$, we would not get a kinetic order (KO) value between 1 and 2. The required condition for that is $n << N$ (low dose sample), so that $A_n N$ becomes much greater than $A_h n$. Thus $F = A_h n / A_n N$ and in (**4.3.2**), n/N gets

replaced by $A_h n/(A_n N)$. In this model, the retrapping terms with the coefficients A_1 and A_2 are taken into account. We solved this system of equations numerically with the help of Mathematica 9.0. Here, A_1, A_2 are the retrapping probabilities, and A_r is the electron-hole radiative recombination probability. The latter one depends on the size of quantum dot. It is clear that the confinement must increase the radiative recombination probability. The coefficient A_r depends on the size of quantum dot. The consideration of retrapping terms with the coefficients A_1, A_2, and A_3 considerably complicates the system of that becomes nonlinear and cannot be solved analytically in general case.

4.4 General order kinetics (May and Partdridge model)

The Randall-Wilkins and Garlick-Gibson forms of the TL equation have been derived with the use of specific assumptions concerning the relative sizes of the retrapping and recombination probabilities. Considering the form of the expressions produced from these assumptions, specifically, May and Partridge [43] wrote an empirical expression for general order TL kinetics: The first or second order kinetics do not explain the actual glow peak, so, in 1964, May and Partridge suggested a general-order expression to cover several cases.

$$I = \frac{dn}{dt} = n^b s' \exp\left(\frac{-E_i}{kT}\right), \tag{4.4.1}$$

where $s^{'}$ and b are the empirical constants called frequency factor (FF) and the kinetic order (KO), respectively. Other quantities have the same meaning as defined before. The intension of proponents of this expression for TL emission which satisfy, for first order(FO) b = 1 and, for second order(SO) b =2. When b is between 1 and 2 or even out side of this range, it is therefore called the general order(GO)kinetics model. Using the same OTOR model as shown for GG model, the general practice now is to

apply it to any experimental glow peak particularly to do the kinetic analysis. This expression, when solved as a function of T gives the equation for the TL glow peak,

$$I = s' n_0^{(b-1)} \exp\Big(-E/kT\Big)\left[1 + \frac{(b-1)s' n_0^{(b-1)}}{\beta}\int_{T_0}^{T} \exp\Big(-E/kT\Big)dT' + 1\right]^{\frac{-b}{b-1}}. \text{[48]} \tag{4.4.2}$$

Chen [44] made a simplification in this equation by assuming $s' n_0^{b-1} = s$. Since the function $s' n_0^{b-1}$ has the dimension s^{-1} like in frequency factor s, Chen assumed its role to be similar to that of frequency factor s in the First order (FO) case. However, to avoid confusing, it with the frequency factor, later workers have designated it as s''. With the above simplification, (4.4.2) becomes

$$I = s'' n_0 \exp\Big(-E/kT\Big)\left[1 + \frac{(b-1)s''}{\beta}\int_{T_0}^{T} \exp\Big(-E/kT\Big)dT' + 1\right]^{\frac{-b}{b-1}}. \text{[48]} \tag{4.4.3}$$

The condition for maximum of TL intensity (T_M) in the glow curve is found by equating the derivative ($\frac{dI}{dT}$)(4.4.3) to zero. The condition turns out as

$$\left[(b-1)\frac{s''}{\beta}\right]\int_{T_0}^{T} \exp\Big(-E/kT\Big)dT + 1 = \left[\frac{s'' b k T_M^2}{\beta E}\right]\exp\Big(-E/kT_M\Big). \text{[48]} \tag{4.4.4}$$

4.5 Method of analysis based on the shape of the glow curve

A popular method of analyzing glow curve in order to evaluate the TL kinetic parameters E, s and b is by considering the shape of the peak. This method essentially uses only three temperature points; namely T_M, T_1 and T_2 ; where T_M, is the peak maximum temperature, T_1 and T_2, are the temperature on the rising and falling side of T_M corresponding to half intensity as shown in Fig. 4.1. This method was developed on the approximation that the glow peak may be described as consisting of two right angle triangles of same height. Order of kinetics depends on the shape factor of the glow peak μ which is in turn related to the temperature T_M, T_1 and T_2 as follows

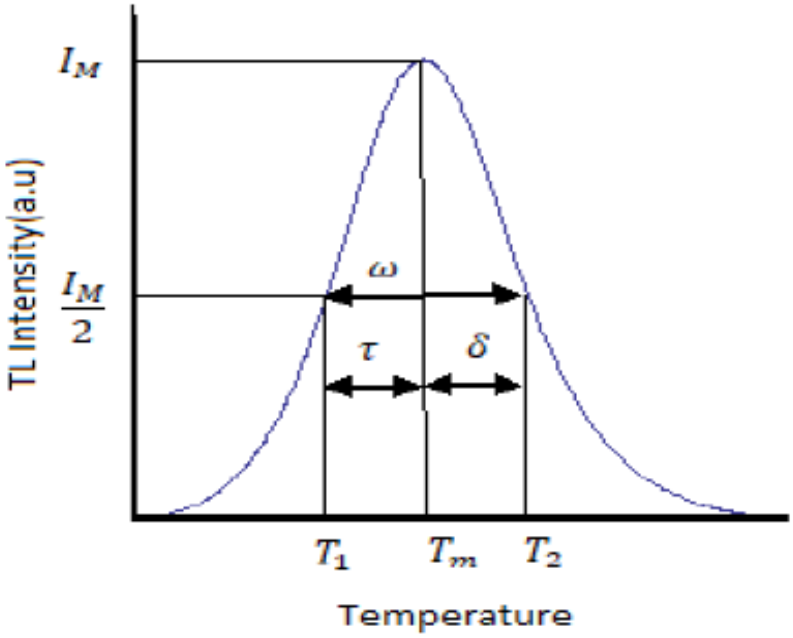

Figure 4.1: The geometrical shape parameters ω , τ and δ.[44]

[28].

$$\mu = \frac{\delta}{\omega} = \frac{T_2 - T_M}{T_2 - T_1}, \tag{4.5.1}$$

where $\omega = T_2 - T_1$ is full width of the full glow peak and $\delta = T_2 - T_M$ is half width towards the fall side of the glow peak and $\tau = T_m - T_1$. First order peak is characterized by $\mu = 0.42$ and a second-order peak by $\mu = 0.52$. For the general case in which kinetic order is not necessarily equal to 1 or 2, Chen [45] investigated the correlation between μ and the three parameters, namely the activation energy, the pre-experimental factor, and the kinetic order. Chen used the glow curve of general order kinetics for this study and found that μ is strongly dependent on order of kinetics and practically independent of the activation energy and the frequency factor.

In fig. 4.1 $\tau = T_m - T_1$ is half width at the low temperature side of the peak. In other words, δ and τ are the width of the two right angle triangles. Another geometric factor γ is defined as $\frac{\delta}{\tau}$. The activation energy is evaluated from Chen's equation for general order kinetic [44,45]. That is;

$$E_\alpha = C_\alpha\left(\frac{kT_M{}^2}{\alpha}\right) - b_\alpha\left(2kT_M\right), [48] \tag{4.5.2}$$

where α represent's ω, τ or δ

$$C_\tau = 1.510 + 3.0(\mu - 0.42), \tag{4.5.3}$$

$$C_\delta = 0.976 + 7.3(\mu - 0.42), \tag{4.5.4}$$

$$C_\omega = 2.52 + 10.2(\mu - 0.42), \tag{4.5.5}$$

$$b_\tau = 1.58 + 4.2(\mu - 0.42), \tag{4.5.6}$$

$$b_\delta = 0, \tag{4.5.7}$$

$$b_\omega = 1. \tag{4.5.8}$$

The possible source of error in this method is that, it is an approximate method in the sense that the value of the peak shape factor μ is not totally independent of the E and s values. In addition, correct measurement of T_M, T_1 and T_2 is essential to get the values of ω, τ and δ.

Moreover, it is important to note that before applying the peak shape method, one should test the glow peak for shift in T_M with change in dose. In case there is no consistent shift, one should assume the glow peaks to belong to the first order kinetics. The thermoluminescence glow curve of small amorphous germanium ($a-Ge$) is obtained at a heating rate of $1C^o/s$. The activation energy is evaluated from Chens equations for general order kinetics (Eqs. 4.5.2 to 4.5.8) [1, 43]. Moreover, the frequency factor s can be calculated using the following equation for general order

kinetics [43]. That is,

$$s = \frac{\beta E}{kT_M^2\left(1 + \frac{2kT_M(b-1)}{E}\right)} \exp\left(-E/kT_M\right), [48] \tag{4.5.9}$$

where β is the heating rate and k is the Boltzmann's constant. The following analytical equation of temperature dependent TL intensity was developed by Kits et. al. [44] for peaks following general order kinetics

$$I(T) = I_M b^{b-1} e^{(\frac{E}{KT}\times\frac{T-T_M}{T_M})}\left\{1+(b-1)\frac{2KT_M}{E}+(b-1)\frac{T^2}{{T_M}^2}\left[1-\frac{2KT}{E}\right]e^{(\frac{E}{KT}\times\frac{T-T_M}{T_M})}\right\}^{\frac{-b}{b-1}} [48]. \tag{4.5.10}$$

The above expression depends on the maximum TL intensity I_M and the temperature corresponding to the maximum TL intensity T_M. In this chapter, the rate equations and the kinetic order model have been discussed. In chapter-5, it is important to analyze the TL emission characteristics the models and factors affecting TL have been discussed in detail to get the mechanisms involved in the process.

Chapter 5

Characteristics of Thermoluminescence Peak Intensities of Germanium Quantum Dots

In this chapter I present the discussion of numerically simulated glow curves of Germanium Quantum Dots. From the graphs I present the detail discussion of the characteristics of TL peaks, specifically peaks shift in relation to temperature, peaks value dependence on activation energy (trap depth), the effect of concentration on peaks height, the effect of frequency factor on glow curve patterns and the TL intensity dependence on heating rates. These stated characteristics will be discussed for first order kinetics, second order kinetics and general order kinetics.

5.1 First order kinetics of Germanium Quantum Dots

Figure 5.1 depicts the graph of TL glow curve as a function of heating temperature. The graph is plotted for first order kinetics using Eq.(4.2.10). As observed from the graphs, as the activation energy increases the peaks shifted to higher temperature side provided other parameters kept constant, but the TL intensity decreases as the

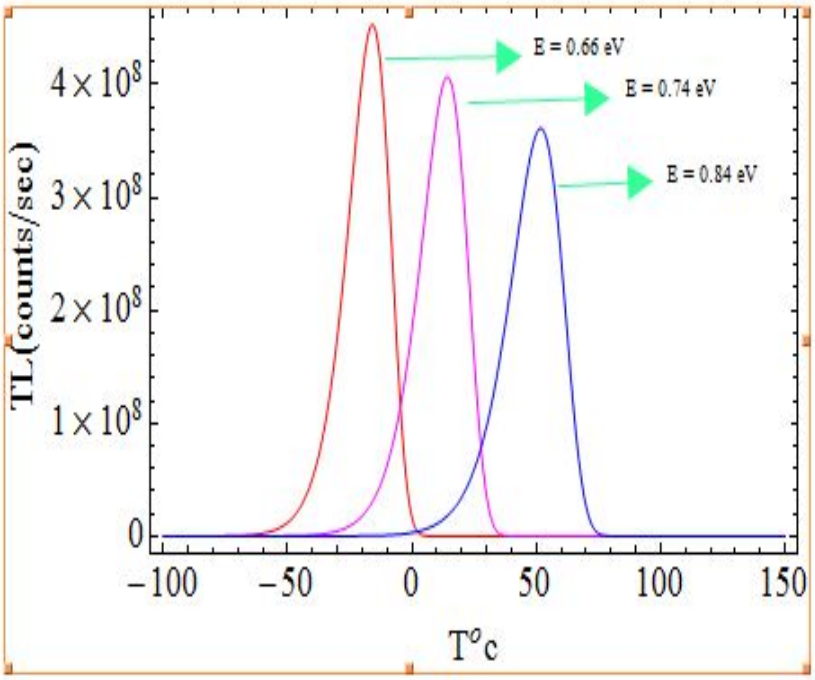

Figure 5.1: First order kinetics TL peaks vs temperature for different value of activation energy and for $n_0 = 10^{10} cm^{-3}$, $S = 10^{12} s^{-1}$, $\beta = C^o/s$. [47]

activation energy increases. For $E = 0.66\ eV$ the temperature related to maximum peak (T_M)is around -30^0C or 243 K, but for $E = 0.84\ eV$, T_M) is around 50^0C or 323 K. The decrease in intensity attributed the recombination of electrons and holes will decrease beyond the band gap.

Figure 5.2 illustrates the TL glow curve of first order kinetics as a function of heating rate, while othere parameters kept constant. The graphs show that when the heating rate increases the TL intensity increases with increase in temperature. The data of Figure 5.2 show that as the heating rate increases, the glow peaks shift to higher temperatures, and the height of the TL peak changes. Because in a typical TL experiment, one collects the TL signal as a function of time, the y-axis in Figure 5.2 is represented in counts/s. These units of counts/s are not suitable for graphing the

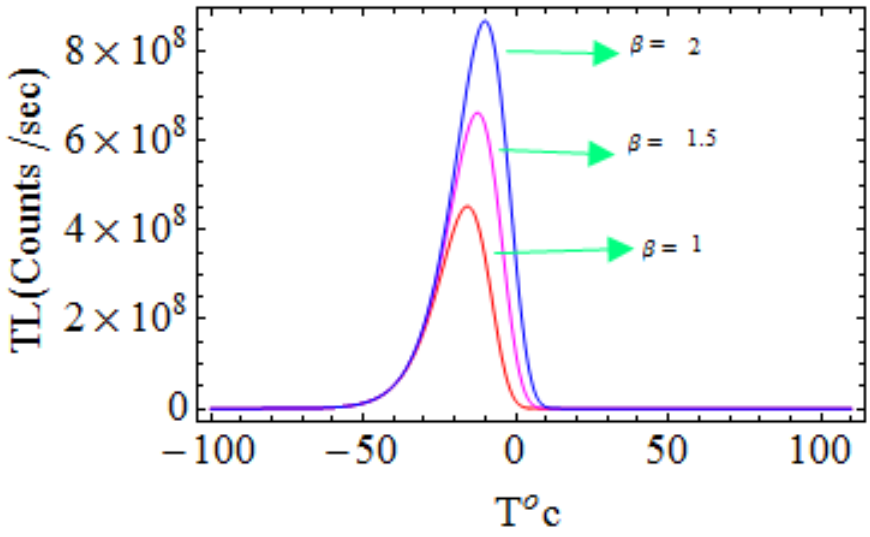

Figure 5.2: First order kinetics TL peaks as a function of temperature for different value of heating rate and for $n_0 = 10^{10} cm^{-3}$, $S = 10^{12} s^{-1}$, $E = 0.66eV$. [47]

actual TL glow curve which is a function of temperature, so it is necessary to convert into temperature units. This is done by dividing each of the graphs in Figure 5.2 by the corresponding heating rate β, and one obtains the y-axis in counts/K. The area under the peaks in Figure 5.2 is proportional to the heating rate β.

Figure 5.3 shows the plots of first order TL peaks versus frequency factor according to Eq. 4.2.10. As seen from the graphs, when frequency factor varies, keeping the other parameters constant, As the value of s is decreased, the TL glow curve shifts toward higher temperatures and at the same time the intensity of TL decrease with decreasing frequency factor.

Figure 5.4 shows the effect of changing the initial concentration of Ge on the shape of TL glow curve and its T_M. As clearly observed from the graphs decreasing the initial concentration of Ge resulted in the decease of TL intensity but there is no shift in T_M value, the symmetric shape of the TL glow curve preserved.

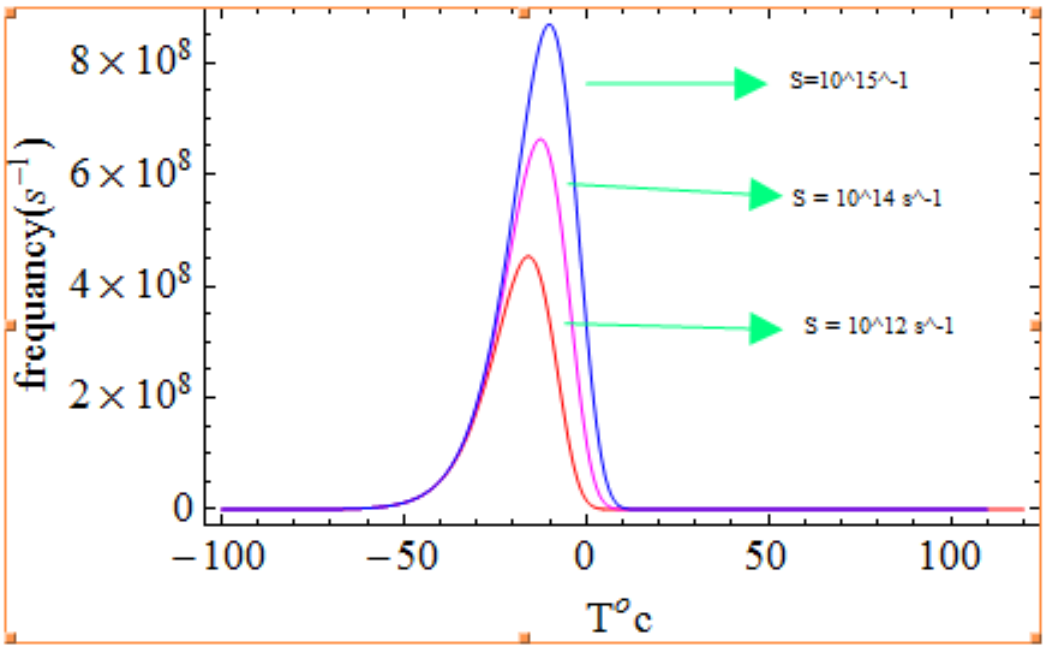

Figure 5.3: First order TL peaks vs temperature for different value of frequency factor and for $n_0 = 10^{10} cm^{-3}$, $\beta = 1 C^o/s$, $E = 0.66 eV$. [47]

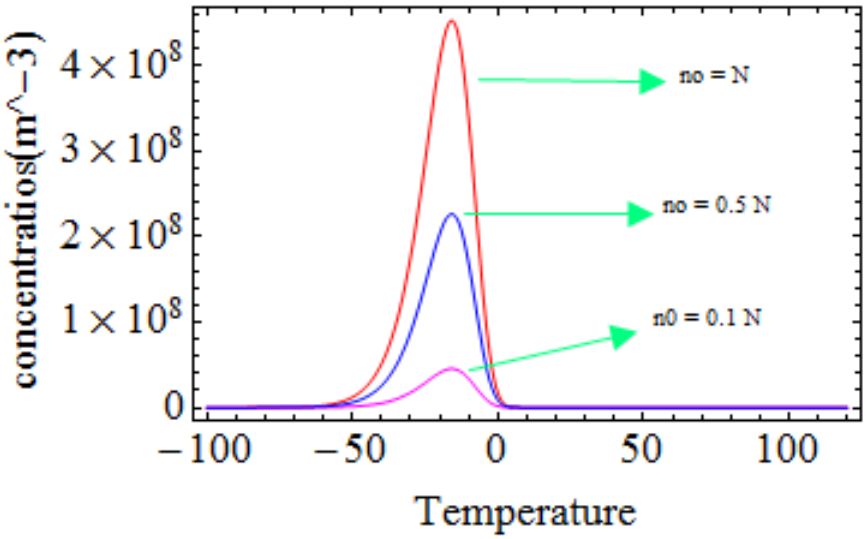

Figure 5.4: First order TL glow curve versus temperature for different value of initial concentration and for $S = 10^{12}s^{-1}$, $E = 0.66\ eV$, $\beta = 1C^o/s$. [47]

5.2 Second order kinetic of Germanium Quantum Dots

Figure 5.5 presents the glow curve of second order kinetics, Eq.4.3.3 Employing the energy band gap of Ge, the TL glow curve intensity decreases with decreasing in the activation energy and shifted to higher temperature region accompanied with increasing of peaks width. Comparing Fig.5.1 and 5.5, one can understand that the peak position shifted to lower temperature region for second order kinetics.

Figure 5.6 depicts the effect of heating rates on intensity TL glow curve for second order kinetics. The result is almost the same as that of first order kinetics except for the present case the position of peaks maxima shifted to lower temperature region. However, the peak hight is proportional to the heating rates.

Figure 5.7 illustrates the TL glow curve for second order kinetics as a function

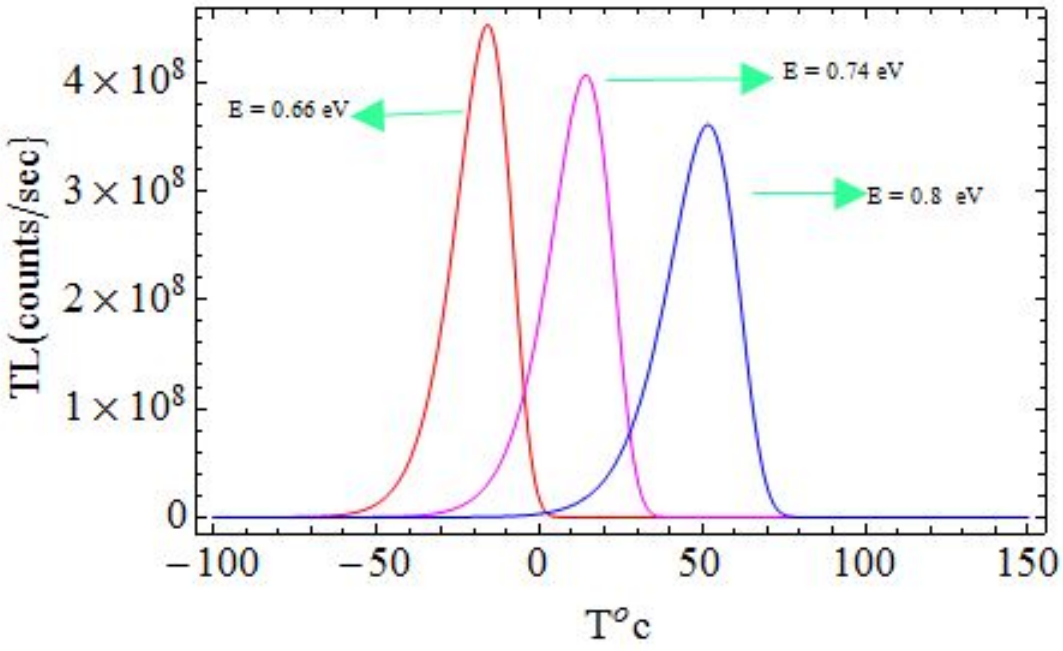

Figure 5.5: Second order TL glow curve versus temperature for different value of activation energy. The parameters used are $N = 10^{12}cm^{-3}$ $n_0 = 10^{10}cm^{-3}$, $S = 10^{12}s^{-1}$, $\beta = 1C^o/s$. [47]

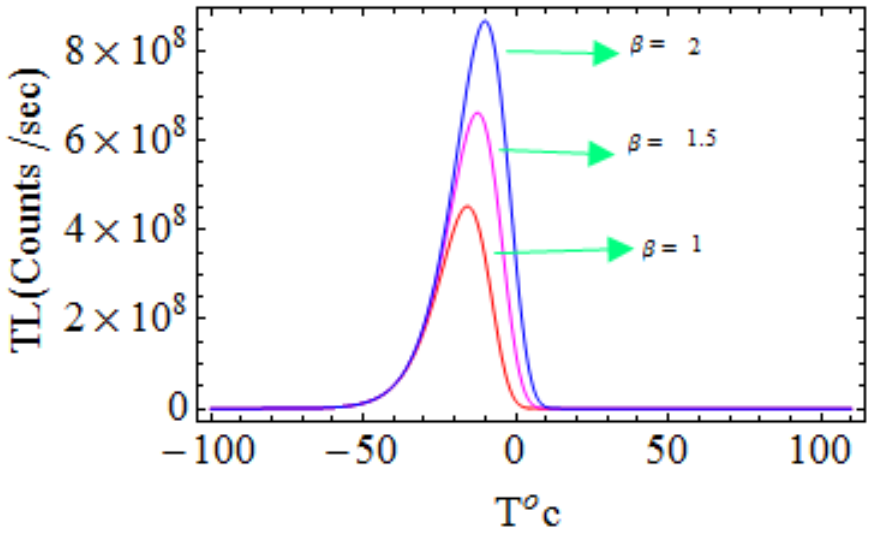

Figure 5.6: Second order TL glow curve versus temperature for different value of heating rate for $S = 10^{12}s^{-1}$, $E = 0.66\ eV$. [47]

of initial concentration. As can be seen from the graphs, with the increase in initial concentration, the TL intensity height increases. However, the maximum peak position shifted to the lower temperature region with increasing initial concentration of trapped electrons.

Figure 5.8 describes the change in TL intensity glow curve as a function of frequency factor, while keeping other parameters constant. From the figure as the frequency factor increases the peak intensity maximum shifted to lower temperature region, and tends to shift lower temperature. For low frequency factor the intensity height gets smaller and the band width gets wider.

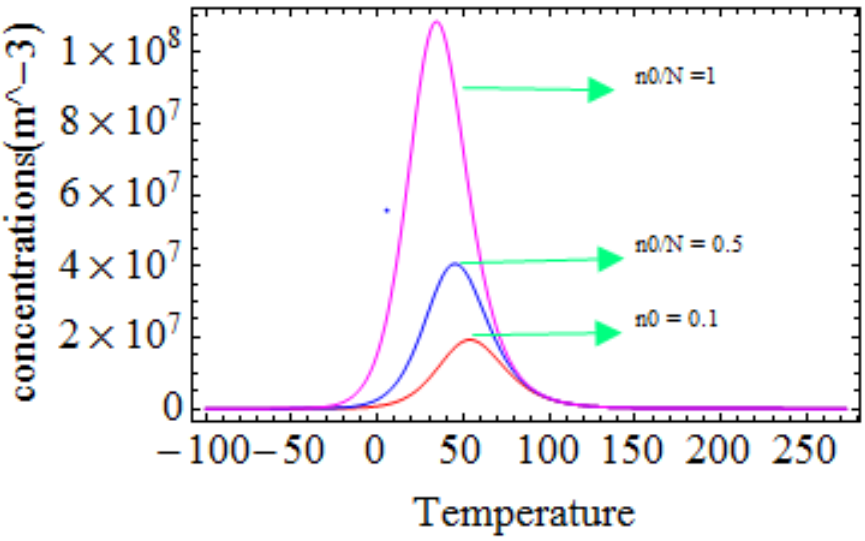

Figure 5.7: TL curve for second order kinetics as a function of initial trapped electrons concentrations: the constant parameters are $n_0 = 10^{12} cm^{-3}$, $S = 10^{12} s^{-1}$, $E = 0.66\ eV$, $\beta = 1 C^o/s$ with initial concentration change. [47]

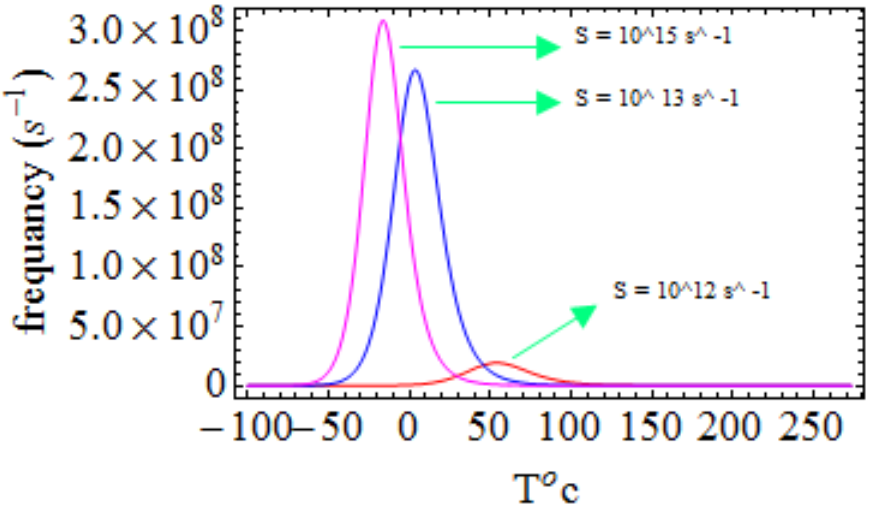

Figure 5.8: TL glow curve dependence on frequency factor for second order kinetics. The constant parameters are $n_0 = 10^{10} cm^{-3}$, $S = 10^{12} s^{-1}$, $E = 0.66\ eV$, $\beta = 1 C^o/s$ and $\beta = 1^0 C/s$.[47]

5.3 General orders kinetics of Germanium Quantum Dots

In this section I can compare the TL intensity of the general order kinetics, when the order parameters b different from 1(the first order kinetics) and 2(the second order kinetics), with the two cases discussed above. The procedures used to plot the TL glow curve is the same as the first order and second order kinetics cases except that the change in the order parameter b.

Figure 5.9 depicts the general order kinetics glow curve as a function of heating rate. The graphs are plotted using Eq. (4.4.2). As the heating rate increases the peak intensity increases but the peaks maxima slightly shifted to higher temperature regions and the TL glow curve width gets wider.

Figure 5.10 illustrates the relation between TL glow curves peaks and shape and

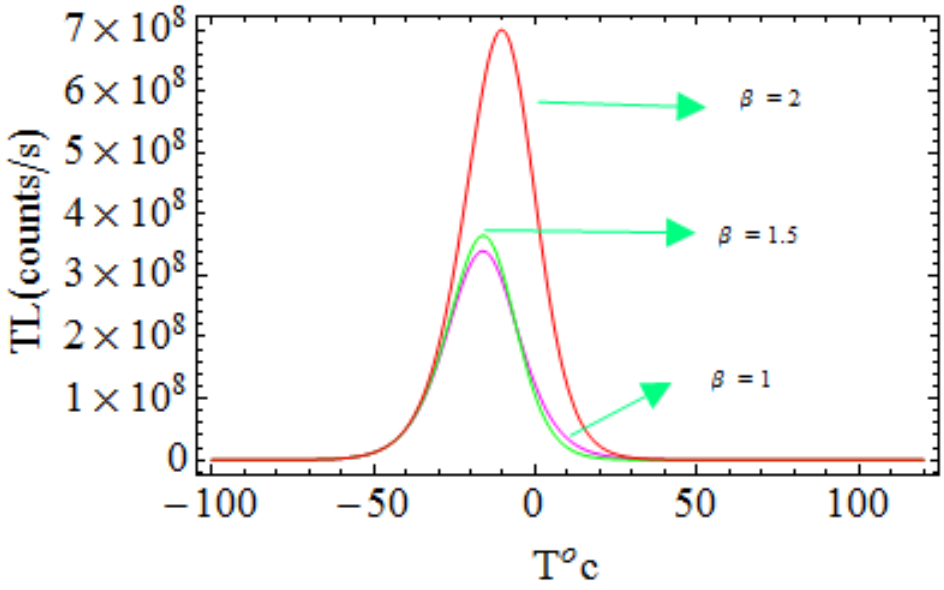

Figure 5.9: General order TL glow curves vs temperature for different value of heating rates. for $n_0 = 10^{10} cm^{-3}$, $S' = 10^{12} s^{-1}$, $E = 0.66\ eV$, $b = 1.5$. [48]

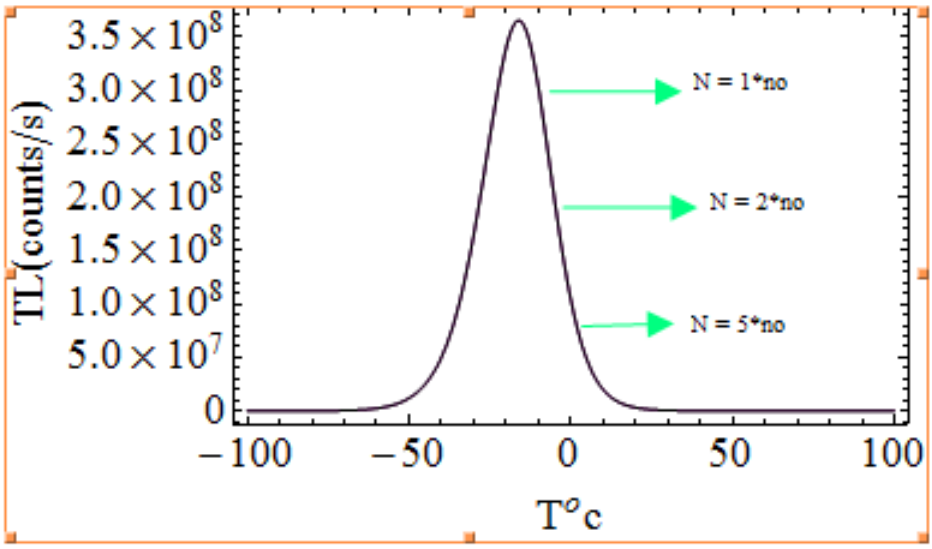

Figure 5.10: TL glow curve for general order kinetics as a function of initial concentration change. for $S = 10^{12}s^{-1}$, $E = 0.66\ eV$, $\beta = 1C^o/s$, $b = 1.5$, $n_0 = 10^{10}cm^{-3}$. [48]

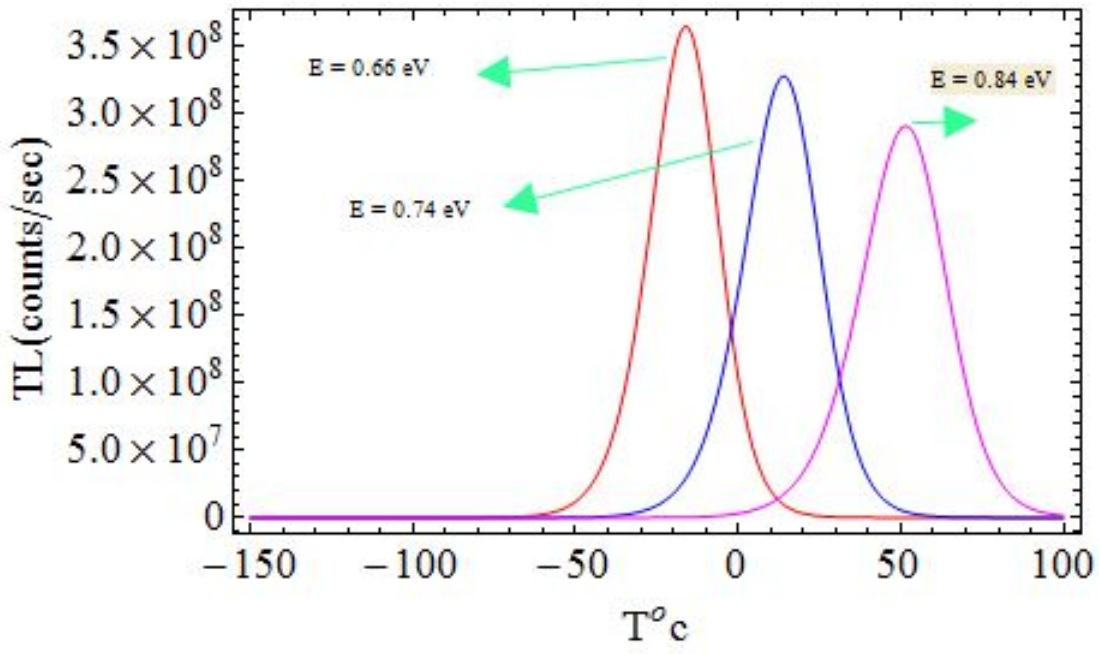

Figure 5.11: General order kinetics peaks $n_0 = 10^{10} cm^{-3}, S = 10^{12} s^{-1}, b = 1.5, \beta = 1C^o/s$ with energy change. [48]

intial concentration of the Ge electron trapped. As it is seen clearly there is no any effect on the peaks intensty, curve shape, and position of T_M.

Figure 5.11 shows the effect of depth energy on TL peaks curve for general order kinetics. The temperature at which the curves attain their maxima in comparison with the first order kinetics case in both it shifted to higher temperature region but to lower side of second order kinetics. But there is no such significant differences in peaks height. Similar to the first and second order kinetics, as the activation energy increased the peaks height decreases and shifted to the higher temperature side.

Finally, Fig.5.12 illustrates the effect of kinetic order b on TL curve peaks and width. As can be seen clearly from the graphs increasing the kinetics order parameter

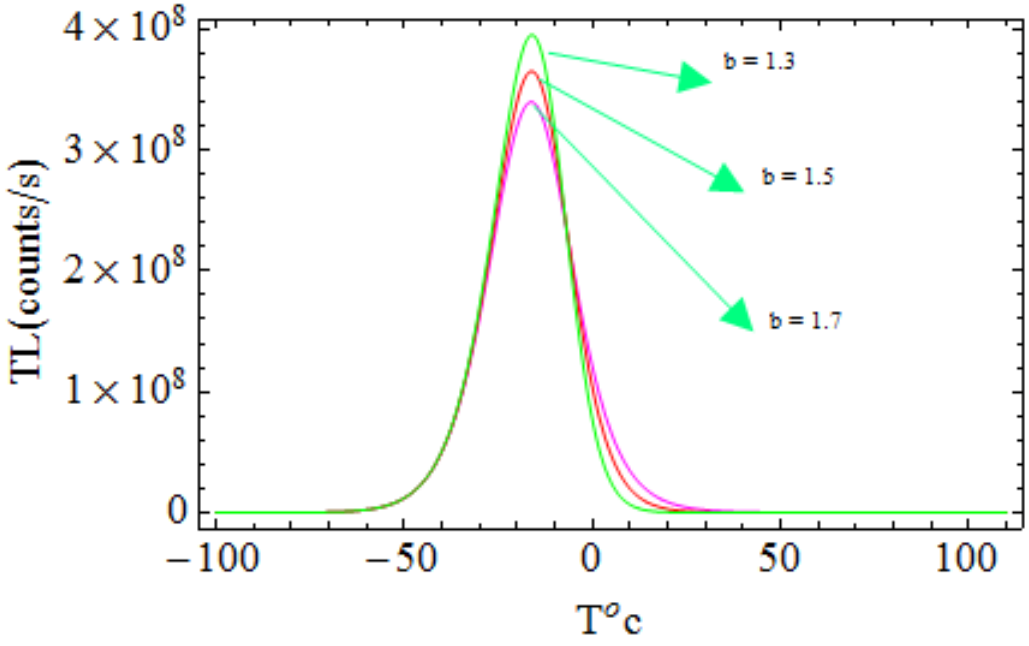

Figure 5.12: General order kinetics peaks $n_0 = 10^{10} cm^{-3}, S = 10^{12} s^{-1}, \beta = 1 C^o/s, E = 0.66 eV$ when kinetic order change. [48]

b result in the decrease of the peak intensity and there is no such significant change in the peaks width. For values of b the TL curves attain maximum peaks for the same temperature values.

5.4 Conclusion

From this study I might draw the following conclusions.

- As the activation energy E is increased, the TL glow curve shifts towards higher temperatures, but the curve maintains its overall shape for the three models.
- The initial concentration of filled traps has no effects on both the maximum height of the TL glow curve and the temperature of maximum TL intensity T_{max}, but leaves the overall shape unchanged in the case of the Garlick-Gibson model and May-Partridge model.
- As the frequency factor s is increased, the TL glow curve shifts towards lower temperatures, but the curve maintains its overall shape for the three models.
- The initial concentration of filled traps has no effects on the maximum height of the TL glow curve, and leaves the shape TL glow curve unchanged.

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