INVESTIGATION OF THERMOLUMINESCENCE FROM AMORPHOUS SILICON QUANTUM DOTS USING THE INTERACTIVE MULTIPLE TRAP SYSTEM MODEL

By

Asamin Regassa

A GRADUATE THESIS SUBMITTED IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE IN PHYSICS AT
ADDIS ABABA UNIVERSITY

ADDIS ABABA, ETHIOPIA
DECEMBER 2018

ADDIS ABABA UNIVERSITY
DEPARTMENT OF PHYSICS

The undersigned hereby certify that they have read and recommended to the Program of Graduate Studies for acceptance a thesis entitled "**Investigation of Thermoluminescence from Amorphous Silicon Quantum Dots Using the Interactive Multiple Trap System Model**" by **Asamin Regassa** in partial fulfillment of the requirements for the degree of **Master of Science**.

Dated: December 2018

Supervisor: _____
Dr. Belayneh Mesfin

Examiners: _____
Dr. Chernet Amente

_____
Dr.Teshome Senbeta

ADDIS ABABA UNIVERSITY

Date: **December 2018**

Author: **Asamin Regassa**

Title: **Investigation of Thermoluminescence from Amorphous Silicon Quantum Dots Using the Interactive Multiple Trap System Model**

Department: **Physics**

Degree: **MSc** Convocation: **December** Year: **December 2018**

Permission is herewith granted to Addis Ababa University to circulate and to have copied for non-commercial purposes, at its discretion, the above title upon the request of individuals or institutions.

Signature of Author

Table of Contents

List of Figures

Acknowledgements

I would like to express my deep gratitude to my advisor and instructor Dr. Belayneh Mesfin for his constant assistance, invaluable guidance, useful discussion, and encouragement without any reservation during the whole period of my study. It was a great pleasure working with him.

I would like to extend my thanks to the Department of Physics of the Addis Ababa University and its staffs. I have learned many things from them like respecting teaching profession, punctuality, encouraging learners to have creative mind and so on.

I would also like to acknowledge the financial support for my studies provided by the Ministry of Education of the Federal Republic of Ethiopia.

Finally, I have received many comments and feedbacks from all my classmates, instructors, and of course many friends. I am very grateful to them not only for their complements but also for their valuable criticism.

Asamin Regassa
Addis Ababa, Ethiopia
December 2018

Abstract

The investigation of the effect of size variation on intensity of thermoluminescence emission from spherical amorphous silicon quantum dots using the model of interactive multi traps system (IMTS) model were studied in this work. The IMTS model consists of one active electron trap (AT), one thermally disconnected deep trap (TDDT), and one recombination centre (RC). Numerical simulations are carried out for quantum dots of diameters 3, 4, 5 ,6 nm to determine TL glow curve and relevant important kinetic parametres. We find that as the size of the Silicon QDs decreases, the intensity of thermoluminescence signal increase, the peak temperatures for each quantum dots is almost remains independent of the size of dots and the TL glow curve looks like first order kinetics. Also, by employing one-trap-one recombination centre (OTOR) model, we showed that the glow peaks of the quantum dots shift towards high temperature values, the widths of the glow curves gets broader and broader with an increase of the dots while the glow curves seems to obey second order kinetics. Furthermore, as the temperature increase; the concentration of electrons $n(T)$ in the AT decreases, the concentration of electrons in the TDDT $m(T)$ increases, and as the quantum dot size increase, concentrations of electrons $n_c(T)$ also increase. In addition the symmetry factor (μ_g), activation energy (E) the order of kinetics (b) as well as the instantaneous concentration of carriers in the traps and recombination centre are numerically simulated. The results obtained may be used while fabricating dielectric compounds enriched in silicon contents for TL applications. Furthermore, it may motivate further theoretical and experimental investigations of the study of the TL phenomena in silicon quantum dots.

Chapter 1

Introduction

1.1 Background the thesis

Thermoluminescence (TL) is the thermally stimulated emission of light following the previous absorption of energy from radiation. The typical glow curve contains one or more glow peaks. Each peak gives information about each trap level and its occupation state, etc in the TL material. The glow peak is analyzed by an empirical method in which a parameter called the order of kinetics is introduced. When the trapped electrons jump up to the conduction band (CB) by the thermal energy, they have two kinds of chances to jump down. One is the retrapping process returning to the same kind of traps and another is the recombination with the hole accompanied by the emission of TL light. When the probability of being retrapped is negligible, the glow curve has a narrow peak shape by a rapid recombination process explained by Randall and Wilkins [1]. Instead, if the retrapping dominates, the recombination with the holes is suppressed and the curve has a wide peak explained by Garlick and Gibson [2]. These two descriptions are called the first-order and second-order kinetics, respectively. Between these two types, the general-order kinetics is introduced for providing a proper analytic continuation from the discrete two types of kinetics explained by May and Partridge [3]. Silicon is a dominant material in micro and nanoelectronics technology, but because of its indirect band structure, it has

not been possible to use silicon as optoelectronics devices such as light emitting diode [1, 2, 3]. The recent advancement in silicon technology has led to the fabrication of zero-dimensional structure, which is called Si nanocrystals, Si nanoparticle, or Si quantum dots (Si QDs) [4, 5, 6]. In quantum dots electrons are confined in all three directions and hence they are known as zero ($0D$) dimensional systems. In fact, these dots are often described as artificial atoms [7, 8] to reflect the importance of quantization phenomena on their properties [9]. The realization of Si QDs system has opened amazingly new area of physical research and technology that deal with atomic scales. Since the active Si QDs have dimensions that are below ten nanometers, the properties of this material completely change for this range of size. Thus, Si QDs systems are considered as potential blocks for future nanoelectronics and nano-photonics [10]. But, in the process of searching for more efficient materials of lower dimension, it has been found that the amorphous silicon quantum dots (a-Si QDs) may be a convenient material for this purpose [11, 12]. In fact, this retains to the bulk a-Si with crystalline silicon (c-Si) [13, 14]; firstly, the luminescence efficiency in a-Si is higher than in c-Si, due to its structural disorder. Secondly, the band gap energy of a-Si (1.6 eV) is larger than that of c-Si (1.1 eV). Therefore, a-Si is believed to be a good candidate for short wavelength light emitters [13, 15].

Due to increasing demands of nanoparticles in semiconductors and optical electronic devices, light emission from such materials got a wide research area in the field of condensed matter physics. The intensity of light emitting devices can be increased with the help of different mechanisms and methods. In particular, the possible increase in the intensity of TL from quantum dots caused by the confinement has been studied in [15]. It was shown that the confinement increases the probability of radiative recombination and enhances the intensity of the TL. The radiative recombination results from a confinement effect which is considered as one of the most effective means to convert an indirect optical band to a direct band. Thus the number of carriers which are recombined radiatively is increasing by decreasing QDs size. In other words, transition between two bands is increased when the size is reduced.

The reduction in dimensionality produced by confining electrons or holes to a thin semiconductor layer leads to a dramatic change in their behaviour. This principle can be developed by further reducing the dimensionality of the electron's environment from a two-dimensional quantum well to a one-dimensional quantum wire and eventually to a zero-dimensional quantum dot. A quantum confined structure is one in which the motion of the carriers (electron and hole) are confined in one or more directions by potential barriers. The efficiency of TL from quantum dots is raised up due to quantum confinement increases the size of the materials and charge carriers the wave functions to overlap effectively.

Wide range of application of TL in different fields like dosimetry for radiation protection and dating of ancient potteries, ceramics, bricks, and geology contributed a lot to the current progress on research related to this field [16, 17]. TL has grown basically as an applied branch of science. It was routinely used to measure UV component of sunlight from the early stage of rocket flights [18, 19]. With the use of different filters including some opaque ones with phosphor packets on board, the rocket produced the direct evidence of the existence of high energy UV components and x-rays in the solar spectrum at high altitudes.

When heat is absorbed from the environment, it decreases the number of trapped electrons by detrapping process. The degree of TL observed from a given sample by filling the localized energy levels with trapped electrons increases the absorption of radiation. On the other hand, the intensity of the TL glow curve 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 understanding and investigation of the TL properties of a material is vital in the development of more efficient materials though many challenges are being faced during fabricating and production of those materials. Thus, selection of a suitable host (defect) material with high chemical durability, thermal and chemical stability are recommended to avoid such difficulties. The following cases must be taken into account to make TL

more efficient for practical use without being different (anomalous) from what is expected or normal reality and emphasis should also be given in theoretical approaches.

• Firstly, using nanostructures, where there is more efficient TL behavior because of quantum confinement effect.

• Secondly, multiple active electron trap levels are considered because of the fact that real semiconductors involve several number of impurities or defect levels below the edge of the CB which act as localized energy levels which are a potential electron or hole traps.

• Thirdly, the free electron in the CB may be trapped several times before recombination with trapped hole.

Therefore, it is necessary to include the rate equations governing the TL kinetics for those cases. Unsolvable rate equations can be solved analytically and the numerical solutions and the simulated results of TL in the IMTS model may be generated with the aid of MATHEMATICA 9 software.

1.2 Objectives of the thesis

In this thesis, we seek to achieve the following objectives:

• investigate the characteristics of TL emission from silicon QDs using the interactive multiple-trap system (IMTS) model,

• examine the effect of size dependent electron-hole recombination probability coefficient (A_h) of Si-QDs on TL glow curves, and

• To determine the important parameters like activation energy, kinetic order, frequency factor, shape factors.

• Make comparsion of the calculated TL kinetic parameters such as the peak temperature (T_m) and the geometrical shape factor of different Si QDs size with models of IMTS and OTOR.

1.3 Layout of the thesis

The thesis is organized as follows: Chapter 2 deals with the theoretical background on luminescence in general and thermoluminescence in particular. The basic concepts of TL as well as different models of TL are discussed in this Chapter. Different methods of analysis of TL glow curves and the different characterization techniques used in this work are explained in Chapter 3. The main results and discussions of the study which include the theoretical and simulated values of TL from silicon QDs in two traps-one recombination center (IMTS) model is studied in Chapter 4. Finally, conclusions are presented in Chapter 5.

Chapter 2

Literature Review

Light is a form of energy. To create the light another form of energy must be supplied. There are two common ways for this to occur, incandescence and luminescence [1, 5]. The spontaneous emission of light upon electronic excitation (e.g., excitation by ultraviolet radiation) is called photoluminescence. Luminescence is a common phenomenon among inorganic and organic as well as in semiconductors and insulators. By studying the luminescence properties we can gain insight not only into the light emission process itself, but also into the competing non radiative photo physical and photochemical processes. Luminescence is the emission of optical radiation (infrared, visible, or ultraviolet light) by matter. The various luminescence phenomena are given their names, which reflect the type of radiation used to excite and to get the emission. The main characteristic of luminescence is that the emitted light is an attribute of the object itself, and the light emission is stimulated by some internal or external process. All hot objects emit light and heat with very similar characteristics and this is well described by models based on a generic black body. To create the light another form of energy must be supplied. There are two common ways for this to occur, incandescence (light from heat energy) and luminescence. In particular, the later type of emission of light and TL are discussed in the next section.

Luminescence is the emission of optical radiation, i.e., infrared, visible, or ultraviolet light, by matter. Luminescence can in occur in a wide variety of matter and under many different circumstances. Thus, atoms, polymers, inorganic, organic or organometallic

molecules, organic or inorganic crystals, and amorphous substances all emit luminescence under appropriate conditions. The various luminescence phenomena are given their names, which reflect the type of radiation used to excite and to get the emission. The main characteristic of luminescence is that the emitted light is an attribute of the object itself, and the light emission is stimulated by some internal or external process. Different models have been discussed in this chapter by many research groups like Randall-Wilkins model, Garlick-Gibson model and May-Partridge model and OTOR and IMTS models. In OTOR model, the peak of the TL intensity corresponding to each peak depends on the level of the trap below the edge of the conduction band; the shallower the trap, the higher the intensity peak. In other words, retrapping has no effect on the intensity peaks. The rate equation governing the TL process and the intensity of the TL in OTOR model are discussed in chapter 2. OTOR model is the simplest model describing a single TL glow peak which consists of one trap and one recombination center. Additional kinetic models have also been suggested, which considers multiple electron traps and recombination centers. It is well-known that the effects of TDDTs can be incorporated in the analysis of TL process by using a set of coupled differential equations. In this type of formulation, a number of models namely (i) One trap one recombination centre (OTOR) model (ii) Interactive multitrap system (IMTS) etc. have been developed to study TL in more detail. In IMTS model, at the time of heating, TDDTs capture free carriers.

2.1 Thermoluminescence

The term thermoluminescence,(TL) is acombination of two words: thermo, meaning heat and luminescence, meaning emission of light. Depending on the type of radiation used to excite the emission, luminescence can be classified into different types. These are photoluminescence, electroluminescence, thermoluminescence, cathodoluminescence, chemiluminescence, bioluminescence, triboluminescence, radioluminescence, ionoluminescence, etc.

Thermoluminescence (TL), also known as thermally stimulated Luminescence (TSL),

is the emission of light from an insulator or semiconductor which is observed when the metastable solid is thermally stimulated [1, 13, 14]. Unlike black body radiation, TL is the thermally stimulated emission of light following the previous absorption of energy from radiation. Three essential conditions are necessary for the production of TL. These are [1, 14]:

• The material must be an insulator or a semiconductor.

• The material must have at some time absorbed energy during exposure to ionizing radiation.

• The luminescence emission is stimulated by heating the material.

In addition, an important property of TL is that once heated to stimulate the light emission, the material cannot be made to emit TL again by simply cooling the sample and reheating. In order to re-exhibit this type of luminescence, the material must be re-exposed to ionizing radiation [1]. It is worth noting that conductors, such as metals, do not exhibit luminescent properties since they lack a band gap.

2.2 Fluorescence and Phosphorescence

In the process of luminescence, when radiation is incident on a material some of its energy is absorbed and re-emitted as a light of a longer wavelength, a process known as Stoke's law. In the process of luminescence, the wavelength of light emitted is characteristics of a luminescent substance and not on the incident radiation. The light emitted could be visible light, ultra-violet, or infrared light. This cold emission, i.e., luminescence, that does not include the emission of black body radiation involve two steps.

• The excitation of electronic system of a solid material to higher energy state.

• Subsequent emission of photons or simply light.

The emission of light takes place at characteristics time τ_c after absorption of the radiation, this parameter allows us to sub-classify the process of luminescence into fluorescence and phosphorescence. The prefix to the term luminescence distinguishes between the modes of excitation, whilst the delay between excitation and emission τ_c distinguishes between

fluorescence and phosphorescence. Thus, if $\tau_c < 10^{-8}$ s, then it is known as fluorescence; whereas if $\tau_c > 10^{-8}$ s, then it is known as phosphorescence, as shown in Fig. 2.1. A large number of substances both organic and inorganic show the property of luminescence, but the principal materials used in various application of luminescence, involves inorganic solid insulating materials such as alkali and alkaline earth halides, quartz (SiO_2), phosphates, borates, and sulphate etc. Luminescence solids are usually referred to as phosphors.

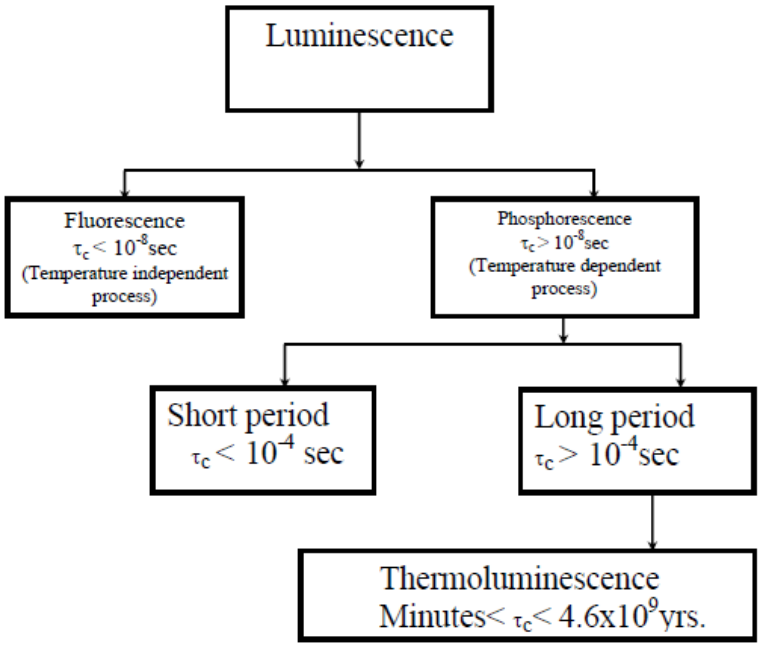

Figure 2.1: Schematic illustration of family tree of Luminescence phenomena.[1]

2.3 Traps and Recombination Centers

The locations where electrons and holes are caught up are called the traps. A hole may be captured at a location where positive charge is lacking or a negative charge is in excess, for example at a positive ion vacancy or at an interstitial negative ion. The binding energy of the trapped charge carrier is called the trap depth or the activation energy of the trap. A recombination center (RC) is defined as an electron or hole trap in which the probability of recombination with an opposite sign charge carrier at the site is greater than that of

thermal excitation of the trapped carrier to its respective delocalized band [22]. Though the presence of impurities in general shifts recombination processes from direct to indirect transitions, it is difficult to predict the effect of individual impurities [23]. The role of an impurity as a trap or recombination center is dependent on the base composition of the material, the other impurities present, the concentration of all impurities, and the oxidation state of the impurities. An impurity that acts as a recombination center in one material will not necessarily act as a recombination center in a different material. Also, a recombination center that results in radiative recombination in a material may produce non-radiative recombination in another material. [23, 24]

An essential feature of all luminescence processes is the change in occupancy of the various localized energy states. These alterations in the population are implemented by electronic transitions from one energy state to another. Several kinds of transition are possible and some are discussed below.

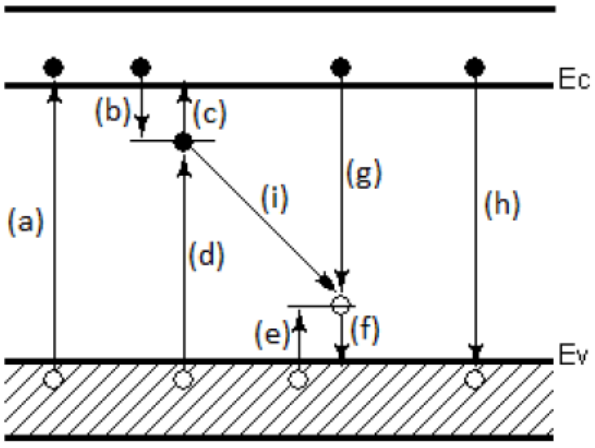

Figure 2.2: Schematic illustration of common types of electronic transitions involving the conduction band (E_c) and valence band (E_v).

The interaction between an incident radiation and atoms in a luminescence material may be described schematically using the energy band diagram, as shown in Fig. 2.2. In the Figure, the letters denote the following processes; (a) ionization, (b) electron (solid circle) trapping, (c) electron release (detrapping), (d) band-to-center recombination; (e)

hole (open circle) trapping, (f) hole release, (g) band-to-center recombination, (h) band-to-band recombination, and (i) center-to-center recombination; respectively.

The primary interaction between ionizing radiation and the electronic structure of atoms is the eventual formation of electron-hole pairs, i.e., transition (a), which can occasionally become trapped as shown in transitions (b) and (e). Through heating, these electrons and holes can be stimulated into migration - transitions (c) and (f), which can lead to electron-hole recombination. If light is emitted during the recombination process, thermoluminescence occurs [1].

2.3.1 Recombination Process

Thermoluminescence is governed by the process of electron-hole recombination. Three distinct types of recombination processes are possible as shown in Fig. 2.2.

• band-to-band - transition (h),

• band-to-center - transitions (d) and (g), and

•center-to-center - transition (i).

The band-to-band recombination is termed direct due to an electron in the conduction band recombining with a hole in the valence band, i.e., an excited electron relaxing to the ground state. The band-to-center and center-to-center recombination processes are termed indirect due to recombination involving localized levels, that is, transitions from or to a trap center. For luminescence to occur, the recombination must be accompanied by the emission of a photon, i.e., it must be radiative [8]. Thus, it becomes necessary to discuss those factors which govern the relative probabilities of direct and indirect, or radiative and non-radiative recombination processes.

• Band-to-band recombination can take place in two ways: (a) If the minimum of the CB and the maximum of the VB occur at the same value of the wave vector, then the transition can take place without momentum transfer and so the process has a relatively high probability; (b) if the band maxima occur at different wave vectors and thus momentum

transfer must take place which gives the band-to-band transition a low probability. Materials for which the energy band extremes coincide type (a) are called direct-gap materials, whilst those of type (b), the more numerous, are called indirect-gap materials.

• The mean time an electron spends in the CB before direct recombination with a free hole in the VB is dependent on the density of excited carriers, on temperature and on the density of recombination sites and is given by;

$$\tau_r = \frac{n_i}{2R} = \frac{1}{2\ n_i\ \tau\ \nu} \qquad \text{and} \qquad R = \tau\ n_i^2\ \nu. \tag{2.3.1}$$

where n_i is the intrinsic free carrier density and R is the temperature dependent rate of direct recombination, τ is the direct-recombination cross-section and v is the thermal velocity of free carriers in conduction or valence bands. This describe that band-to-center recombination mechanism may be dominant, particularly at low temperatures. At higher temperatures the measured lifetimes are often seen to approach those expected for band-to-band transitions.

• The introduction of impurities and other lattice defects results in luminescence emission of wavelengths which are longer than those expected from conduction to valence band transitions, showing a shift from direct (band-to-band) to indirect (band-to-center) recombination. Narrow band-gap specimens show a greater tendency for direct recombination.

• The luminescence efficiency of a phosphor, η, is related to the probability of a luminescence transition, P_r, and the probability of a non-radiative transition, P_{nr} is given by;

$$\eta = \frac{P_r}{P_r + P_{nr}}. \tag{2.3.2}$$

This describes whether or not a material (phosphor) will exhibit luminescence following irradiation and the absorption of energy, depends upon the relative probabilities of the radiative and non-radiative transitions [1].

An additional route by which the excited electron can return to its ground state is suggested in the configurational coordinate diagram. If the electron absorbs an amount of

thermal energy ΔE, it can now transfer easily to the ground state without the emission of radiation, but with just the dissipation of heat causing the return of the electron to the minimum energy. From this discussion the probability of a non-radiative transition of Eq. 2.3.2 is related to the temperature by a Boltzmann factor $\exp\left(\frac{-\Delta E}{kT}\right)$. The radiation probability P_r is unaffected by temperature, thus Eq. 2.3.2 may be rewritten as;

$$\eta = \frac{1}{1 + c\ \exp\left(\frac{-\Delta E}{kT}\right)} \tag{2.3.3}$$

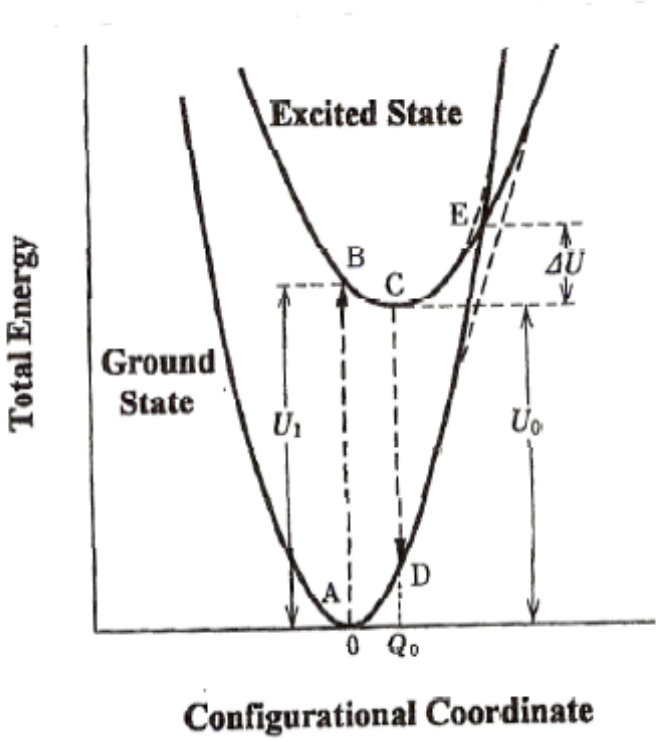

Figure 2.3: Possible variations of electron energy with configurational coordinate for excited and ground states in a semiconductor or insulator. The two curves are modified by repulsion near the intersection (broken lines). The vertical broken lines A to B, B to A and C to D and D to C indicate the absorption and emission of light, respectively.

2.3.2 Direct and Indirect Transitions

In a direct transition Fig. 2.4, the excited electron must lose an amount of energy corresponding to the band gap. As this would require the simultaneous creation of many

phonons, or phonon-like excitations in the case of non-crystalline materials like glass, to dissipate the electron's energy, it is unlikely that this energy could be totally dissipated by phonon interaction alone which would be required for a non-radiative transition. Therefore, photons are emitted during band-to-band transitions, and the transitions are radiative [1, 5, 21].

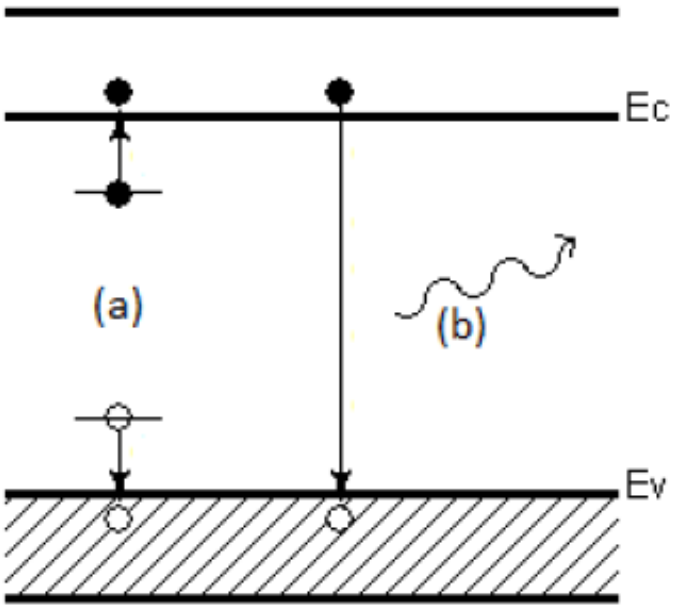

Figure 2.4: Direct recombination transition (band-to-band): (a) the electron (solid circle) and hole (open circle) are stimulated back to the conduction (Ec) and valence (Ev) bands; (b) the electron and hole recombine and a photon is emitted.

In an indirect transition shown in Figs. 2.5, the energy dissipated is much less than the band-gap. The energy, therefore, may be dissipated either radiatively via photons or nonradiatively via phonons [1]. A material's relative probability of direct versus indirect transitions and radiative versus nonradiative processes for indirect transitions, therefore, has a strong influence on the amount of luminescence the material will exhibit.

2.3.3 Center-to-Center Recombination

Center-to-center recombination offers additional pathways for de-excitation as shown in Fig. 2.5. If a trapped electron and hole are situated close to each other in the material,

recombination can take place through tunneling as in transition (a). Alternatively, an electron can be elevated to a higher energy level, then recombination can take place through tunneling as in transition (b) followed by transition (c). These pathways can be radiative or non-radiative [1].

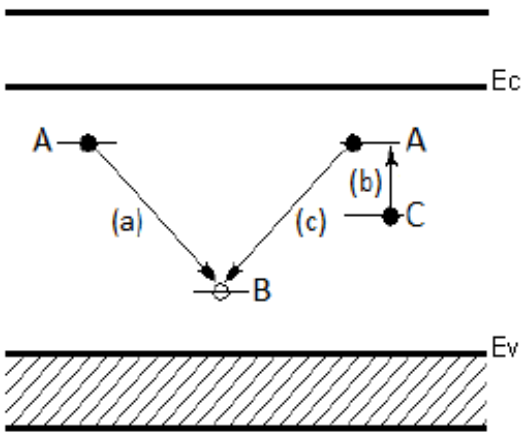

Figure 2.5: Indirect recombination transitions not involving the conduction or valence bands (center-to-center): (a) an electron (solid circle) at level A recombines with a hole (open circle) at level B through tunneling; (b) an electron at level C is raised to level A, then (c) recombines with a hole at level B through tunneling.[1]

2.4 Models of Thermoluminescence

The thermoluminescence from different materials has been studied by many research groups using different models like Randall-Wilkins model, Garlick-Gibson model and May-Partridge and OTOR and IMTS models. In OTOR model, the peak of the TL intensity corresponding to each peak depends on the level of the trap below the edge of the conduction band; the shallower the trap, the higher the intensity peak. In other words, retrapping has no effect on the intensity peaks.

The OTOR model is the simplest model describing a single TL glow peak which consists of one trap and one recombination center. Additional kinetic models have also been suggested, which considers multiple electron traps and recombination centers. It is well-known that the effects of TDDT's can be incorporated in the analysis of TL process

by using a set of coupled differential equations. In this type of formulation, a number of models, namely, (i) one-trap-one-recombination center (OTOR) model, (ii) interactive multi-trap system (IMTS) etc. have been developed to study TL in more detail. In IMTS model, at the time of heating, TDDT's capture free carriers.

2.4.1 Simple Thermoluminescence Model

The process by which materials emit light when heated can be understood by considering the simplest possible model consisting of two localized levels: (i) an isolated electron trap labelled as b and (ii) a recombination center labelled as R; and hence the model is commonly called one-trap-one-recombination center model (OTOR); shown in Fig. 2.6. There are two delocalized bands, conduction band (CB), and valence band (VB), in this energy band found just two localized level, one behave as a recombination center, and the other behave as a trap. The activation energy or trap depth (E) is defined as the distance between the trap and the bottom of the CB. In a valence band, if the electron absorption of radiation of energy ($h\nu > E_g$), producing free electrons and holes (see Fig. 2.6). The free carriers may either recombine with each other, become trapped or remain free in their respective delocalized bands.

Moreover, Fig. 2.6 shows the effect of heating, when the free electron absorbs enough energy, it to be released back into the conduction band, from where recombination is possible and accompanied by the release of a light emission [2], where a is the generation of holes and electrons, b is the electron trapping, the c is hole trapping, the d is electron release by heating, the R is recombination center with light emission, E is the activation energy or trap depth, g is hole trap depth, E_f is Fermi level and thus empty in the equilibrium state, and E_g is forbidden energy.

If N denotes the total concentration of the traps in the crystal (m^{-3}), by $n(t)$ the concentration of filled traps in the crystal in m^{-3} at time t, and $n_h(t)$ is the concentration of trapped holes in the recombination center in m^{-3} and the initial concentration of filled traps at time $t = 0$ is denoted by n_0 then the intensity of the emitted light is equal to the

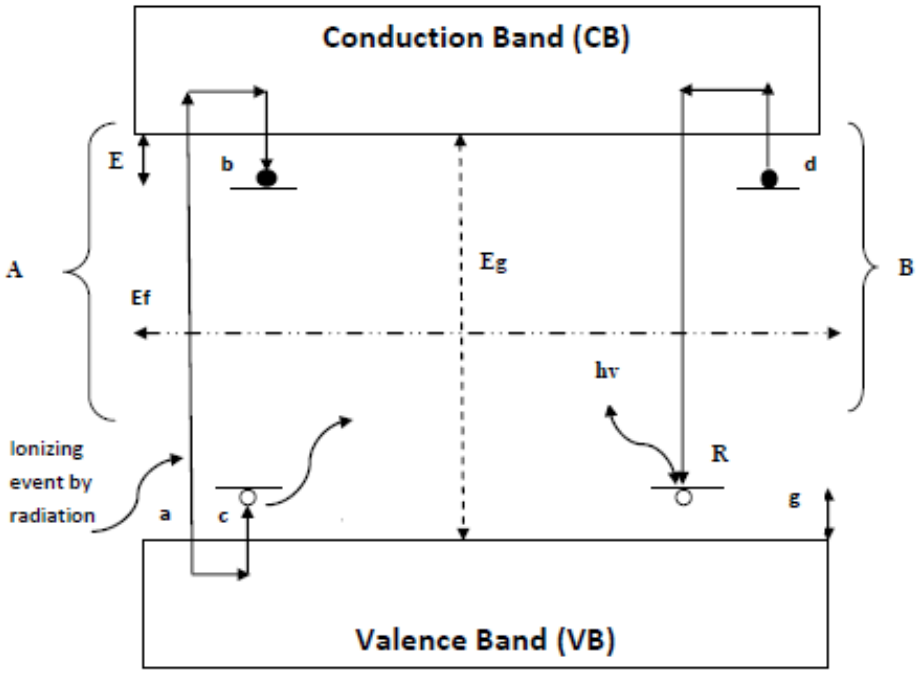

Figure 2.6: Simple two-level model for thermoluminescence. Open and closed circles are hole and electron, respectively.

rate of recombination of holes and electrons in the recombination center and is given by;

$$I(t) = \frac{dn_h}{dt}, \tag{2.4.4}$$

where $I(t)$ is the intensity of TL emission. In a typical thermoluminescence experiment the sample is heated with a linear heating rate $\beta = dT/dt$ from room temperature up to a high temperature usually around 500 ^0C. As the temperature of the sample is increased, the trapped electrons in the trap are thermally released into the conduction band.

A simple energy level scheme consisting of one type of traps and one type of recombination centers (OTOR) is shown in Fig. 2.6. The traps are assumed to be of electron type and the recombination centers (RC) of hole type. The traps and the RC get filled up by the respective type of charge carriers during irradiation. During heating the electrons are ejected out of the traps and become free to move in the conduction band. During the random motion if the electron comes across an oppositely charged defect center called the

RC it may recombine with it and emit luminescence. Alternatively, it may fall back into an empty trap (see Fig. 2.6). This is called retrapping. The transport of the electrons from the traps to the RCs to emit luminescence may be described in terms of rate of these three components. These three rates for the OTOR model are given by;

$$R_{ex} = ns \exp\left(\frac{-E}{kT}\right), \tag{2.4.5}$$

where R_{ex} is the excitation rate and the retrapping rate, R_{ret} is given by

$$R_{ret} = n_c A_n (N - n), \tag{2.4.6}$$

and the recombination rate, R_{rec} is given by

$$R_{rec} = n_c A_h n_h, \tag{2.4.7}$$

where N and n are the total and the filled concentration of the thermally active traps, n_c is the concentration of the charge carriers in the free state, n_h is the concentration of the available RC, E is the activation energy of the trap, which is also called the trap depth, T is the sample temperature, k is the Boltzmann constant and A_n and A_h, respectively, are the retrapping and the recombination coefficients. The values of these coefficients depend on the electron capture cross sections σ_n and σ_h of the traps and the RC, respectively:

$$A_n = \sigma_n v \qquad \text{and} \qquad A_h = \sigma_h v, \tag{2.4.8}$$

where v is the free electron velocity in the conduction band. The value of n_h depends on the physical scheme used in formulating any particular model of TL. For the models which are based on the OTOR scheme h is equal to n.

Essentially the value of n_h is the sum of all the filled traps in the sample, which means the filled active traps n and any deeper level traps which are thermally not affected, at the given temperature T. The equality between the value of n_h and sum of all the filled traps ensures the overall charge neutrality of the sample. It is assumed that all the excited charge carriers relax from their free state instantly either into the RC or alternatively into the empty traps, with no significant number of these being left behind in the free

state (conduction band when the charge carriers are electrons). This is called the quasi-equilibrium (QE) condition. We may see that the expressions for R_{ex} and R_{ret} would be the same for the various models of TL. The expression for R_{rec} alone would change with the model used. Considering the relaxation probabilities R_{ret} and R_{rec}, the fraction F of the excited carriers which produces luminescence during heating is given by;

$$F = \frac{R_{rec}}{R_{rec} + R_{ret}}. \tag{2.4.9}$$

Depending on the values of the parameters in Eqs. (2.4.5)- (2.4.8), the value of F would change. If there are additional routes of relaxation, for example nonradiative recapture in deeper level traps, these would add to the denominator in Eq.(2.4.9). The expression for F would thus changes according to the applicable physical model.

2.4.2 Randall and Wilkins Model

Randall and Wilkins were the first to suggest a theoretical model for the TL emission. They assumed that the retrapping may be negligible ($R_{ret} = 0$) and therefore according to Eq. (2.4.9), we have $F = 1$. This means that the TL emission intensity I is directly proportional to R_{ex}.

$$I = cR_{ex} = -\frac{dn}{dt} = cn \exp\left(\frac{-E}{kT}\right), \tag{2.4.10}$$

where $T = T_0 + \beta t$ and where c is a constant representing the optical efficiency factor relating the luminescence output to the electron release rate and the measuring instrument's efficiency to collect the light. We may take $c = 1$, since it makes no difference to the characteristics like the shape of the glow curve and its decay pattern. It influences only the intensity. Since the electrons in the traps have a Maxwellian distribution of thermal energies, the probability per unit time of electron escaping from a trap depth E below the CB is

$$P = s \exp\left(\frac{-E}{kT}\right). \tag{2.4.11}$$

If there are n electrons in traps at a time t then from equation

$$dn = -nP = -sn \exp\left(\frac{-E}{kT}\right) dt. \tag{2.4.12}$$

Assume that the sample is warmed up at a linear rate of heating, so that $\beta = dT/dt$ in Ks^{-1}. Equation (2.4.12) may be written as

$$\frac{dn}{n} = -\frac{s}{\beta}\exp\left(\frac{-E}{kT}\right)dT. \tag{2.4.13}$$

Upon integration of the above equation we obtain the value of n at any temperature T during heating through;

$$n = n_0 \exp\left[-\int_{T_0}^{T}\frac{s}{\beta}\exp\left(\frac{-E}{kT'}\right)\,dT'\right], \tag{2.4.14}$$

where n_0 is the initial number of trapped charges and T_0 is the temperature at the beginning of the heating run. Substituting Eq. (2.4.14) for n in Eq. (2.4.10), we obtain the expression for TL intensity, as a function of temperature T as:

$$I(T) = n_0 s \exp\left(-\frac{E}{kT}\right)\exp\left[-\int_{T_0}^{T}\frac{s}{\beta}\exp\left(\frac{-E}{kT'}\right)\,dT'\right]. \tag{2.4.15}$$

Equation (2.4.15) is the expression of the glow curve. The initial part of the glow curve rises exponentially. In this part, the change in n is not perceptible. On the other hand, the probability of thermal excitation P given by $s\exp(\frac{-E}{kT})$. The value of n may be considered constant at n_0 in this part. This property is useful to determine the value of trap depth E using the initial rise method. When the number of trapped charges n, is appreciably diminished, the TL intensity curve ceases to rise in the exponential fashion. It goes through a maximum before falling and ultimately falls to zero when all the traps are emptied.

The intensity I at any temperature T in the glow curve is equal to the product of the values of n and P at that temperature. The intensity I being directly proportional to n this model of TL comes under the category of first order kinetics. The characteristics of the glow curves of this model are;

• The glow curve is asymmetric, rising comparatively slowly and falling somewhat sharply.

• The glow peak shifts to higher T as E increases. Higher value of E means stronger binding of the trapped charge. Hence, it is understandable that a higher temperature is needed to release it. It is seen that with increase in the value of E the peak height is reduced,

but the peak half width ω, is increased, thus maintaining the area constant for a given value of n_0.

• The temperature of maximum intensity, T_m increases almost linearly with E.

• For given values of E and b, the glow peak shifts to lower T as s is increased. Thus, E and s have opposite effects on T_m. This is simple to understand since higher s means faster escape of the trapped change from the excited state of the trap. Higher s leads also to increase in peak height and to reduction in the peak width ω.

• For given values of E and s, the peak temperature T_m increases as heating rate b is increased. When b is increased the glow peak becomes narrower and taller, with area being conserved, When the value of I is plotted against T, the peak recorded with higher b increases in height as well as in area. However, when the height is normalized with b the area gets conserved. The experimental intensity values for different b agree with the theory if the luminescence of the sample does not suffer thermal quenching at higher heating rates.

• The glow peak characteristics, namely the peak temperature T_m and the peak shape remain unchanged when the initial filled concentration n_0 of the traps is changed. This means that the peak characteristics are independent of radiation dose given to the sample. However, the intensity (the area as well as the height of the peak) increases in direct proportion to n_0 for given E, s and b. This means that the intensity is directly proportional to dose given to a sample, assuming that the trap filling is directly proportional to the dose.

These characteristics are unique to FO kinetics and are of prime importance in the application of TL in radiation dosimetry as well as in kinetics analysis of the glow curves.
Remarks: The initial concentration of filled traps (n_0) affects only the maximum height of the TL glow curve, and leaves the shape of the first-order TL glow curve and the temperature of maximum TL intensity (T_m) unchanged.

2.4.3 Garlick and Gibson Model

Garlick and Gibson modified the model of Randall-Wilkins for the TL intensity using the same 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 Randall-Wilkins 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 OTOR model 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,

$$F = \frac{A_h n}{A_h n + A_n(N-n)}. \tag{2.4.16}$$

Garlick and Gibson assume that the excited charge carrier has no particular preference for recombination or retrapping which means$A_h = A_n$. Thus we get $F = n/N$. In contrast to this, the F value in RW model is equal to 1. We now see that the intensity $I(T)$ of luminescence given by Eq. 2.4.10 would be modified by a factor equal to n/N. Thus in Garlick and Gibson model, the intensity becomes;

$$I(T) = -\frac{dn}{dt} = s\frac{n^2}{N}\exp\left(\frac{-E}{kT}\right). \tag{2.4.17}$$

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 $dt = dT/\beta$, integration of Eq. 2.4.17 yields the value of n at any temperature T. Multiplying that value of n by the escape probability $p = s\exp(-E/kT)$, gives the equation for glow curve viz

$$I(T) = n_0^2\frac{s}{N}\exp\left(\frac{-E}{kT}\right)\left[1 + \frac{n_0 s}{\beta N}\int_{T_0}^{T}\exp\left(\frac{-E}{kT}\right)\,dT'\right]^{-2}. \tag{2.4.18}$$

It is worthwhile to mention here that second-order kinetics is obtained in OTOR model even if $A_h \neq A_n$. The required condition for that is $n \neq N$ (low dose sample), so that

A_nN becomes much greater than A_hn. Thus, $F = A_hn/A_nN$ and in Eq. 2.4.18, n/N gets replaced by A_hn/A_nN and in Eq. 2.4.17 , s/N gets replaced by sA_h/A_nN. It is to be remembered that in the case of $A_h \neq A_n$, the SO kinetics is obeyed only in low dose samples ($n \neq N$), whereas the Garlick and Gibson model of SO kinetics is valid at all doses. The characteristics of first order kinetic glow curves may be described as follows:

• The fall of the glow curve is slightly slower than its rise. This is in contrast to the FO kinetics case in which the fall is faster than the rise. The average value of the shape factor for different E and s has been found to be 0.52 in contrast to 0.42 in the case of FO kinetics [29].

• For a given set of parameters E, s, b and n_0/N the temperature of maximum intensity T_m is on the higher side as compared to that of the FO, except when $n_0 = N$ (traps filled to saturation), in which case the T_m for the FO and the SO kinetics is nearly same.

• The glow peaks shift to higher temperature and become progressively wider in shape as the value of n_0/N is reduced, i.e., smaller is the dose, higher the T_m and wider are the peaks. This is in contrast to the FO kinetics case in which T_m and shape factor are independent of n_0/N.

The other properties, namely the dependence of T_m on E, s and b as expected, are similar to that of the FO kinetics case. At this point it is worthwhile to elaborate on the term kinetic order (KO) which we would be using frequently while discussing different models to describe the TL emission process.

Remarks: The initial concentration of filled traps (n_0) affects both the maximum height of the TL glow curve and the temperature of maximum TL intensity (T_m), but leaves the overall shape unchanged.

2.5 Order of Kinetics in Thermoluminescence Theory

In thermoluminescence theory, the term order of kinetics has been taken from chemistry. It is related to the rate of chemical reaction and the change in the concentration of

reactants.

2.5.1 First and Second Order Kinetics

The term 'first-order kinetics' in TL theory refers to the case in which the rate is directly proportional to the concentration of one reactant (Glasstone and Ldewis 1960). In the first theoretical account of TL, Randall and Wilkins [2] showed that a TL peak resulting from a single electron trapping state and a single kind of centre results in first-order kinetics if one assumes no re-trapping of the electrons released. When the rate of a chemical reaction is directly proportional to the change in the concentration of only one of the reactant, it is called mono molecular kinetics or first order kinetics. However, if the rate of chemical reaction is directly proportional to the change in the concentration of both the reactants, it is called bi-molecular kinetics or second order kinetics. The reaction following second-order kinetics may be written as;

$$\frac{dn}{dt} = Cn(t)m(t), \tag{2.5.19}$$

where C is constant $n(t)$ is instantaneous electron occupancy and $m(t)$ is instantaneous trap occupancy.

In the FO kinetics, the electron retrapping probability is assumed to be zero and the TL intensity I at any temperature T during heating stage depends only on the concentration n of electrons in the active traps at that temperature. Randall and Wilkins demonstrated that a TL glow curve corresponding to a single electron trapping state and a single kind of recombination center results in first-order kinetics if there no retrapping of the detrapped electrons. The equation describing this process was, thus,

$$\frac{dn}{n} = -s \ \exp\left(\frac{-E}{kT}\right) \ dt. \tag{2.5.20}$$

2.5.2 General-Order Kinetics

May and Partridge suggested a more general expression for TL emission which would satisfy not only the FO and SO kinetics expressions when $b = 1$ and $b = 2$, respectively,

but would also include all other possible values of b including its non-integral values between 1 and 2 or even outside this range. Accordingly, they proposed the following expression for TL intensity

$$\frac{-dn}{dt} = n^b s' \exp\left(\frac{-E}{kT}\right), \tag{2.5.21}$$

. where s' and b are the empirical constants called frequency factor and the order of kinetics, respectively. Therefore, this expression for TL intensity is called general order kinetics. There is a general practice of applying Eq. (2.5.21) to any experimental glow peak to do kinetic analysis though it is based on OTOR model. This is under the assumption that it includes all plausible physical schemes that may be applicable to the glow peaks. The solution of Eq. (2.5.21) gives the following temperature dependent expression for the TL glow peak:

$$I(T) = n_0^b s' \exp\left(\frac{-E}{kT}\right)[1 + \frac{(b-1)n_0^{b-1}}{\beta}\int \exp\left(\frac{-E}{kT}\right)dT']^{\frac{-b}{b-1}}, \tag{2.5.22}$$

where $b > 2$. Eq. (2.5.22 was simplified by under the assumption that $s = s'n_0^{b-1}$. The role of $s'n_0^{b-1}$ was assumed to be similar to that of the frequency factor in the first-order kinetics mainly because of the fact that it has the dimension s^{-1} like the frequency factor. However, to avoid confusion, later workers have designated it as s'' instead of s. Therefore, Eq. (2.5.22 becomes,

$$I(T) = n_0 s'' \exp\left(\frac{-E}{kT}\right)[1 + \frac{(b-1)}{\beta}\int \exp\left(\frac{-E}{kT}\right)dT']^{\frac{-b}{b-1}}. \tag{2.5.23}$$

2.5.3 Mixed-Order Kinetics

The expression of the general order kinetics discussed above is only empirical a better alternative (expression) which fit neither in first-order nor second-order is required in dealing with TL glow peaks. To fill this gap, the mixed order kinetics was originally proposed by Visocekas, Chen [29] have further elaborated on the model proposed by Visocekas and suggested that mixed order kinetics has merit over general order kinetics since it is derived from a physically meaningful model whereas the general order kinetics

is only empirical. The equation for the mixed order glow curve when the linear heating rate of $\beta = dT/dt$ is used is given by;

$$I(T) = s'C^2\alpha \exp\left[\frac{s'C}{\beta}\int \exp\left(\frac{-E}{kT}\right)\right] \exp\left(\frac{-E}{kT}\right)\left\{\exp\left[\frac{s'C}{\beta}\int \exp\left(\frac{-E}{kT'}\right)dT'\right] - \alpha\right\}^{-2} \tag{2.5.24}$$

where α is the kinetic order parameter in mixed order kinetics and is defined as $\alpha = n_0/(n_0 + C)$ and C is the population of the thermally disconnected deep traps (TDDTs). The TDDTs may be assumed to be totally filled, so that they do not capture the carriers liberated from the active traps during heating. In its most general form the OTOR is described by the following coupled differential equations as;

$$\frac{dn}{dt} = -sn \exp\left(\frac{-E}{kT}\right) + A_h n_c(N - n), \tag{2.5.25}$$

$$\frac{dn_c}{dt} = \frac{-dn}{dt} = A_h n_c(n + n_c), \tag{2.5.26}$$

$$\frac{dn_h}{dt} = \frac{dn}{dt} + \frac{dn_c}{dt}, \tag{2.5.27}$$

$$I_{TL} = \frac{-dn_h}{dt} = A_h n_c(n + n_c), \tag{2.5.28}$$

where E is thermal activation energy of the trap (eV), s is the frequency factor (s^{-1}), T is the temperature of the sample (K), k is Boltzmann constant (eVK^{-1}), N is the total concentration of the traps in the crystal (cm^{-3}), n is the concentration of filled traps in the crystal (cm^{-3}), n_0 is the initial concentration of filled traps at time $t_0(cm^{-3})$, A_n is the probability coefficient of electron retrapping in the traps (cm^3s^{-1}), A_h is the probability coefficient of electron recombining with holes in the RC (cm^3s^{-1}). In addition, $n_c(t)$ and $n_h(t)$ represent the instantaneous concentrations of the electrons and holes in the conduction band and RC, respectively.

2.5.4 Interactive Multi-Trap System

The model consists of two trapping states and a RC, as shown in Fig.4.1. The first trap is considered to be the one responsible for TL (denoted as the active trap (AT) below), and the second trap is denoted as the thermally disconnected deep trap (TDDT) that dealing with a glow curve with single peak. The two traps are characterized by total concentrations N and M, and by instantaneous occupancies $n(t)$ and $m(t)$, respectively. Because of the conservation of charge in the crystal, the concentration of holes in the RC at any moment must be equal to the total instantaneous concentration of electrons $n + m + n_c$. When the competitor trap is saturated, that is, when $m_0 = M$, the IMTS model is known as the non-interactive multiple trap system (NMTS). On the other hand, in the absence of the competitor traps, i.e., when $M = 0$, the IMTS model becomes the OTOR model [1, 5]. More on this section in chapter four.

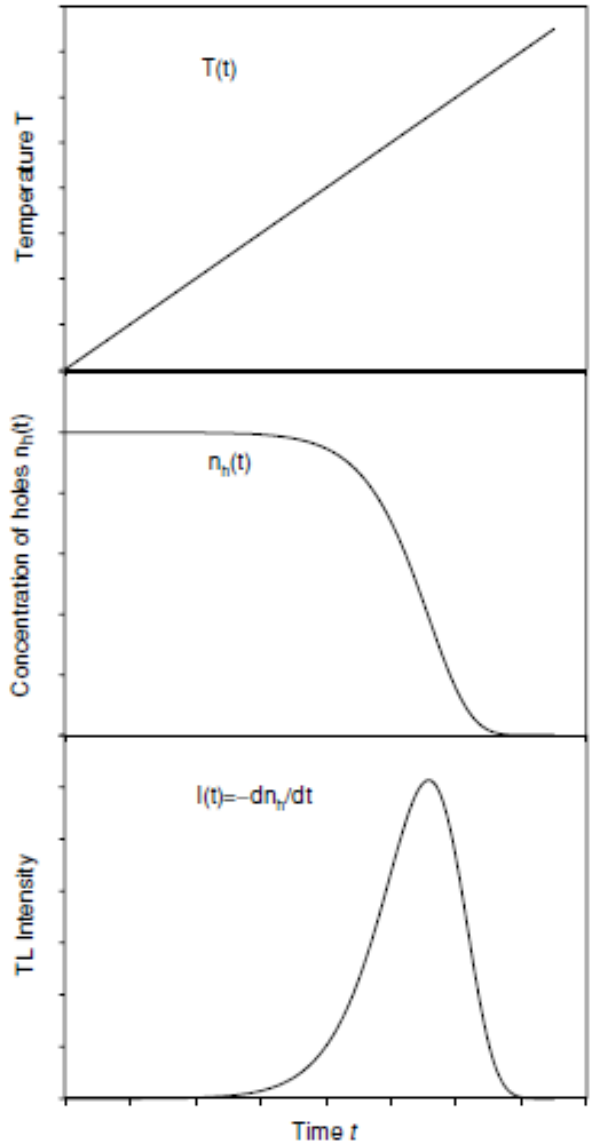

Figure 2.7: The temperature profile $T(t)$, the thermoluminescence intensity $I(t)$, and the concentration of trapped holes $n_h(t)$ in the recombination center RC as a function of time t. A linear heating rate β is assumed.

Chapter 3

Methods of Analysis of Thermoluminescence Glow Curves

The individual TL glow curves of a materials can be analyzed by using different techniques in order to determine the kinetic TL parameters, such as the activation energy E, the frequency factor s and the order of kinetics b. The purpose of glow curve analysis essentially is to find the activation energy E and the kinetic order b of the given glow peak. In a practical situation the quantities of interest are the temperature T_m where the maximum TL intensity I_m occurs, and the shape factor δ or width of the TL glow curve. Some of these methods like initial rise method (to determine E), first approximation of E, method that uses only the initial rising portion of a glow peak (the whole TL glow curve method), peak Position Methods (Methods of Analysis Based on the Temperature at the maximum and method of analysis based on various heating rate), method of analysis based on the shape of the glow curve used in this paper are discussed in this chapter.

3.1 Initial Rise Method

This method is commonly used to determine the activation energy when only one glow peak is presented and analyzed. However, when the glow peak is more complex, a wide peak and some holders appear in the structure, the application of the initial rise method is not valid since multiple trapping levels are considered and then the thermoluminescence analysis becomes difficult to perform. The underlying principle in this method is that the

dependence of the amount of trapped electrons $n(T)$ is negligible in the low temperature tail of TL glow peak and it can be assumed to be approximately constant. In other words, very little detrapping will take place at this low temperature region indicating that this method is independent of the order of kinetics. With rise in temperature, the first exponential in Eq. 3.6 increases, whereas the value of the second term remains close to unity and this remains valid when the TL intensity I has risen by no more than 15% of the maximum intensity of the glow peak I_m. The second term in equation Eq. 3.2.6 decrease with further increase in temperature $T > T_C$ and the competition between the two terms in this equation results in the peak shape of the TL glow curve.

The intensity in the initial part of the glow curve may be expressed as,

$$I(T) \propto \exp\left(\frac{-E}{kT}\right). \tag{3.1.1}$$

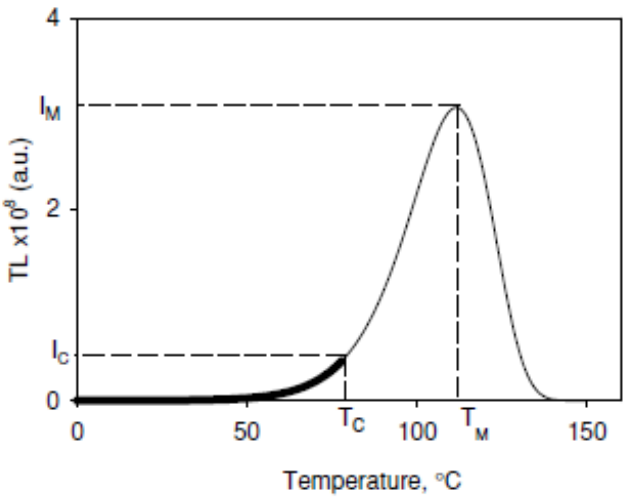

Figure 3.1: The initial rise part of a thermoluminescence glow curve.

Figure 3.1 depicts the initial rise part of a single TL glow peak. In using this method, a graph of $\ln(I)$ versus $\frac{1}{kT}$ is made and a straight line of slope $-E$ is obtained. The activation energy E is evaluated from the slope of this line without any knowledge of the frequency factor [4] proposed a graphical approach as alternative method and is shown in Fig. 3.2. By using a point I_C on the isolated TL glow peak and drawing the tangent at

the point $N = (T_C, I_C)$, the slope can be calculated;

$$I(T) = C \exp\left(\frac{-E}{kT}\right). \tag{3.1.2}$$

By taking the derivatives of Eq.(3.1.2) $I(T)$ is given by:

$$\frac{dI}{dT} = C\frac{E}{kT^2}\exp\left(\frac{-E}{kT}\right) = I\frac{E}{kT^2}. \tag{3.1.3}$$

The slope tangent at a point N is obtained by setting $T = T_C$ in Eq. (3.1.3) it yields;

$$\frac{dI}{dT} = I_C\frac{E}{kT_C^2}. \tag{3.1.4}$$

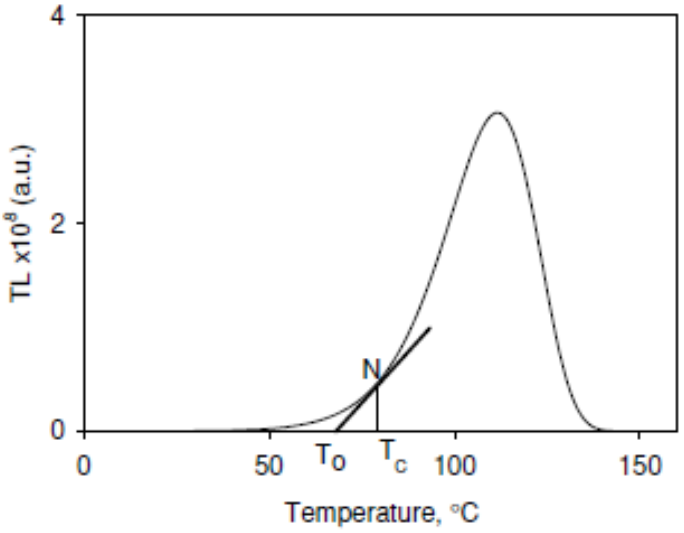

Figure 3.2: The graphical method proposed by Ilich.

In order to determine the point $M = (T_0, 0)$, where the graph intersects the x-axis, the following equation of the tangent line is used,

$$I - I_C = \frac{I_C E(T - T_C)}{kT_C^2}. \tag{3.1.5}$$

Using $I = 0$ in Eq. (3.1.5) gives;

$$E = k\frac{T_C^2}{T_C - T_O} \tag{3.1.6}$$

A large number of points (T_C, I_C) can be selected and statistically processed in order to improve the reliability of the results of this method. Therefore, Eq. 3.1.6 gives the

estimated value of the activation energy. In recent years, the initial rise method was extended to multiple trapping levels in thermoluminescent materials. The quantity E_{eff} corresponding to an average value over the E_i values of each single sub-level is taken into consideration as a consequence, the trapping parameter s, which is of course considered as an effective value, is calculated once E_{eff} is obtained.

The following precautions should be made while using this method. (a) The initial rise part of the glow peak under study should be free from any contribution from any nearby glow peaks, and (b) There should be no lag in temperature between the heater plate and the sample and no temperature gradient across the sample thickness. This means that the sample layer should be very thin and it should be firmly deposited on the heater pan. Use of slow heating rate is desirable to avoid temperature lag between the heater pan and the sample. Therefore, though this method can be applicable to any order of kinetics, it is not applicable if the resolution of the TL glow peak is poor due to the presence of nearby overlapping peaks.

3.2 First Approximation of E(Heuristic Method)

These are the first approximations for the evaluation of activation energies. However, the accuracy expected in these methods is, in general, poor. From TL experiments, D. Curie [1, 3, 4] deduced the following empirical relation between the activation energy (E) and the maximum temperature of the glow peak T_m for a given value of β/s.

$$E = \frac{T_m - T_0}{k}. \tag{3.2.7}$$

3.3 The Whole Thermoluminescence Glow Curve Method

Unlike the initial rise method that uses only the initial rising portion of a glow peak, this method uses the number of data points which may be used to calculate E is severely limited. This may be overcome by using not just one small section of the curve but the

whole peak (the whole or total glow peak method) and this enables E, s and the kinetic order b, to be calculated. Thus, this method is also known as 'area method' or 'whole glow peak' method of analysis, and is based on the measurement of the integral under a glow peak. It can be applied when a well isolated and clean peak is available. It is possible to estimate the value of the integral $n(T)$ of the TL intensity over a certain temperature region using the area under the glow curve between a given temperature T_0 in the initial rise region, up to the final temperature T_f at the end of the glow peak, as shown in Fig. 3.3.

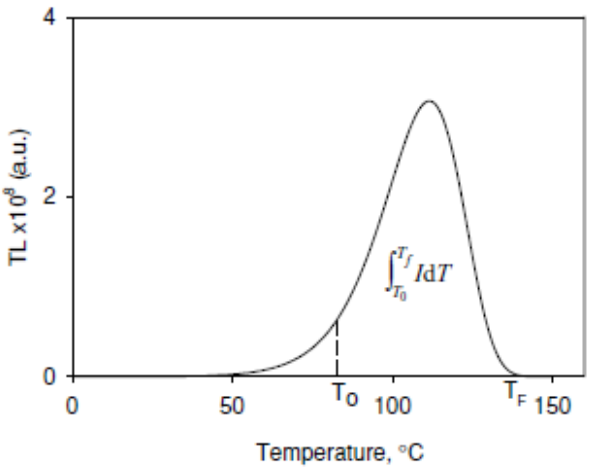

Figure 3.3: Calculation of the area $n(T)$ in the whole glow peak measurement method.

$$n = \int T\ dt = \frac{1}{\beta}\int I\ dT \tag{3.3.8}$$

Taking it first order kinetics and substituting the Randall-Wilkins relation the following relation can be obtained.

$$\ln\left(\frac{I}{\int I\ dT}\right) = \ln\left(\frac{s}{\beta}\right) - \frac{E}{kT}. \tag{3.3.9}$$

This equation shows that in the case of first-order kinetics the term $\ln(I/n(T))$ is a linear function of $1/kT$, with a slope $-E$ and an intercept equal to $\ln(s/\beta)$. May and Partridge [1, 6] and Muntoni et al proposed the same method in the case of general order

kinetics. In this case the equation takes the form

$$\ln\left(\frac{I}{n^b}\right) = \ln\left(\frac{s'}{\beta}\right) - \frac{E}{kT} \tag{3.3.10}$$

which is graphically processed by plotting $\ln(I/nb)$ versus $1/kT$. If the kinetic order b is known, one can obtain a broad range of temperatures in which the curve is a straight line. When the kinetic order is unknown, several lines are drawn with various values of b and the best straight line is chosen.

3.4 Peak Position Methods of Analysis

These methods fall under two broad categories, estimation methods based on the location of maximum TL intensity T_m, and methods which employ variable heating rates during measurement of the TL glow peaks.

3.4.1 Methods of Analysis Based on the Temperature at the Maximum

Randall and Wilkins [46] did not solve the FO equation, but they considered the maximum temperature of the TL glow peak as corresponding to a temperature slightly below that in which the probability of an electron escaping from the trap is equal to unity. These authors found a very simple expression for E, using a value of $s = 2.9 \times 10^9\ s^{-1}$;

$$E = 25\ kT_M \tag{3.4.11}$$

and[49]gave a similar relation using $s = 10^9 s^{-1}$;

$$E = \frac{T_M}{500} = 23\ kT_m. \tag{3.4.12}$$

The numerical factors in both Eqs. 3.4.11 and 3.4.12 are dependent upon the s value, and hence the values of E are only approximate. These equations can be used only as a first approximation of the E-values.

3.5 Methods of Analysis Based on Various Heating Rates

It is the most widely used method for the analysis of TL glow curves. When the linear heating rate β changes, the temperature T_m of the maximum TL intensity of the peak also changes: faster heating rates produce a shift in temperature toward higher values of T_m. This effect is shown in Fig. 3.4. Bohum, Porfianovitch and Booth proposed a method of calculating E based on two different heating rates for a first-order peak. Considering the maximum condition and using two different heating rates, one gets;

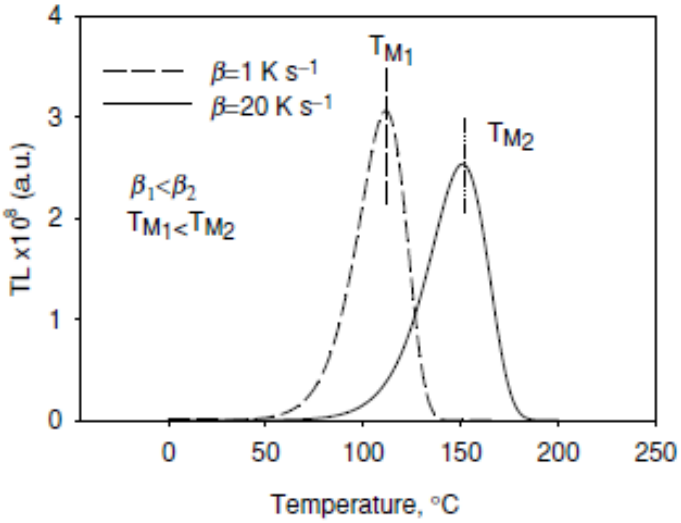

Figure 3.4: The change in the temperature T_m of maximum intensity with the heating rate.

$$\ln\left(\frac{T_m^2}{\beta}\right) = \ln\left(\frac{E}{sk}\right) + \frac{E}{kT_m} \tag{3.5.13}$$

The resultant plot of $\ln(T_m^2/\beta)$ versus $1/kT_m$ should yield a straight line with slope E and an intercept $\ln(E/sk)$.

3.6 Methods of Analysis Based on the Shape of the Glow Curve

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, respectively, are the temperatures on the rising and falling side of T_m corresponding to half intensity as shown in Fig. 3.5. A popular method of analyzing a TL glow curve to find out definitely the kinetic parameters E, s, and b is by considering the shape or geometrical properties of the peak. TL glow peaks corresponding to second order kinetics are characterized by an almost symmetrical shape, whereas first order peaks are asymmetrical. One defines the following parameters shown in Fig. 3.5. The method was developed on the approximation that the glow peak may be described as consisting of two right angled triangles of same height. Order of kinetics depends on the shape factor of the glow peak δ which is in turn related to the temperatures T_m, T_1 and T_2 as:

$$\mu = \frac{\delta}{\omega} = \frac{T_2 - T_m}{T_2 - T_1}. \tag{3.6.14}$$

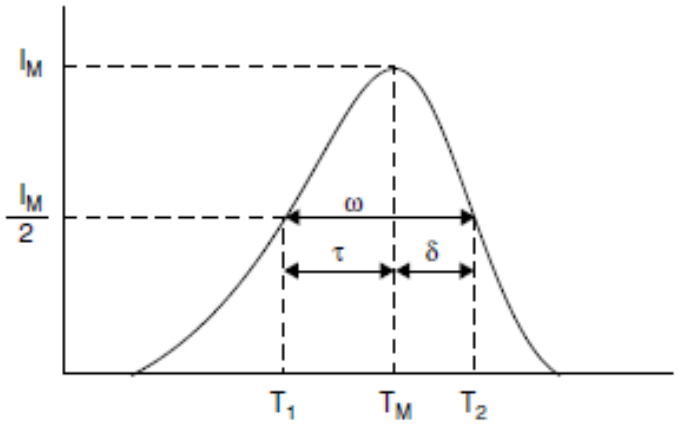

Figure 3.5: The geometrical shape quantities τ, δ, ω.

where T_m is the peak temperature at the maximum, T_1 and T_2 are respectively the temperatures on either side of T_M corresponding to half intensity, $\tau = T_m - T_1$ is the half-width at the low temperature side of the peak, $\delta = T_2 - T_m$ is the half-width toward

the fall-off side of the glow peak, $\omega = T_2 - T_1$ is the total half-width and $\mu = \frac{\delta}{\omega}$ is the so-called geometrical shape or symmetry factor.

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, [1, 6, 12] investigated the correlation between μ and the three parameters, namely the activation energy, the pre-exponential factor and the kinetics order. Chen used the glow curve of general order kinetics for his study and found that μ is strongly dependent on the order of kinetics and practically independent of the activation energy and the frequency factor. The computations covered values of the kinetic order between 0.7 and 2.5, the activation energy between 0.1 and 1.6 eV, and the frequency factor between 10^5 and 10^{19} s^{-1}. The result is shown in Fig. 3.6 and it is used to find the value of the order of kinetics from the measured value of γ in an experimentally measured glow peak. In Fig. 3.6, $\tau = T_m - T_1$ is the half width at the low temperature side of the peak. In other words, δ and τ are the widths of the two right angled triangles. Another geometrical factor is defined as $\frac{\delta}{\tau}$. The activation energy is evaluated from Chen's equations for general order kinetics. That is,

$$E_\alpha = C\alpha(\frac{T_m^2}{\alpha}) - b_\alpha(2kT_m) \tag{3.6.15}$$

where α represents τ, δ or ω.

$$C_\omega = 2.52 + 10.2(\mu - 0.42), \tag{3.6.16}$$

$$C_\tau = 1.510 + 3.0(\mu - 0.42), \tag{3.6.17}$$

$$b_\tau = 1.58 + 4.2(\mu - 0.42), \tag{3.6.18}$$

$$c_\delta = 0.976 + 7.3(\mu - 0.42), \tag{3.6.19}$$

$$b_\delta = 0, \qquad b_\omega = 1. \tag{3.6.20}$$

with $\mu = 0.42$ for the case of first-order(FO) TL glow peaks, and $\mu = 0.52$ for the case of second-order (SO) peaks. 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. The purity of the glow peak is an essential requirement for the accuracy of the results. In addition, correct measurement of T_m, T_1 and T_2 is essential to get the values 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, as stated earlier, one should assume the glow peaks to belong to the first order kinetics.

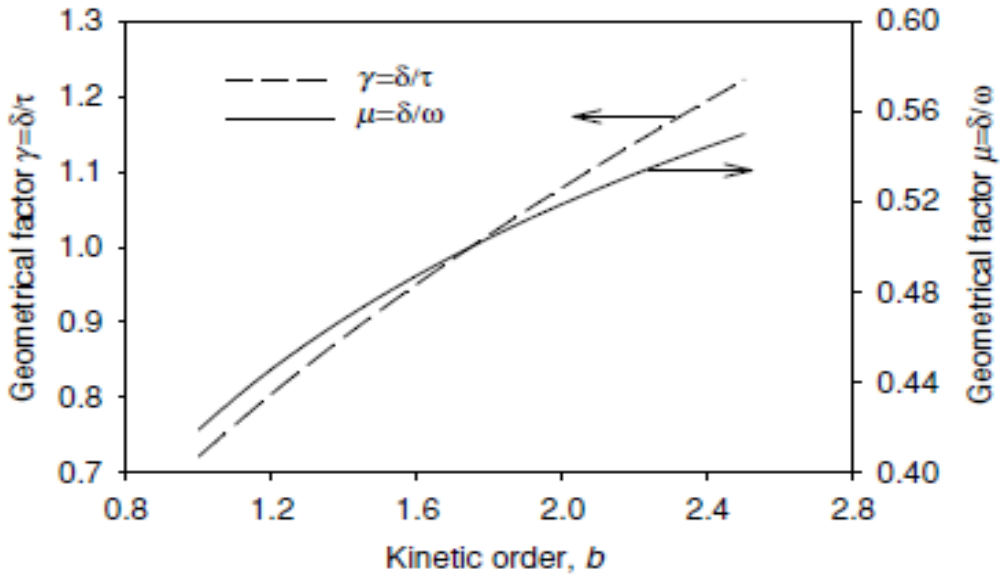

Figure 3.6: Relationship between the kinetic order b and the geometrical factors $\mu = \frac{\delta}{\omega}$ and $\gamma = \frac{\delta}{\tau}$.

Chapter 4

Results and Discussion

Interactive multi-trap system is an energy level scheme which includes both the active traps (that is traps which are getting thermally excited at a given temperature during recording of TL glow) and the thermally disconnected deep traps(TDDT). In this scheme the TDDTs recapture the electrons which have been ejected out from the active traps during the heating to read the TL. The basic representative of this model is that, in addition to the main active dosimetric trap, it contain thermally disconnected deep traps (TDDT) and there are more than one active electron traps taking part in TL process and the glow peaks formed depends on the retrapping situation. These TDDT are considered to be thermally stable during the TL experiment. The charge carriers released from the AT during heating may be recaptured in the TDDT. In this work we consider IMTS model for our investigation of the TL properties from QDs [4, 12].

4.1 Electrons Rate Equations for The Model

In our investigation, the rate equations used consists of one active electron traps AT, one thermally disconnected deep trap TDDT, and one recombination center RC as shown in Fig. 4.1. From the figure, it is assumed that in the process of traps or centre filling is already attained with prior irradiations of the sample by ionizing radiations. During trap emptying, electrons trapped in AT trap may be released from it (transition from AT to

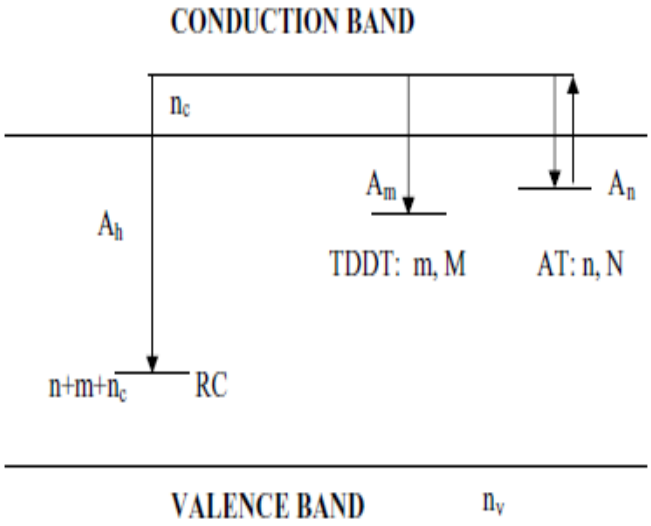

Figure 4.1: Energy level diagram consisting of one type of active electro trap(AT), one type of recombination center (RC) and one thermally disconnected deep trap (TDDT). The upward or downward directed arrows indicate the possible electron transition during read- out

conduction band) by thermal stimulation of energy comparable to the activation energy, E of the trap. Subsequently, these thermally elevated free electrons are released back from the conduction band either to recombine with the holes in the recombination center RC(i.e, transition from conduction band to RC) yielding luminescence, or end up being retrapped in the AT or TDDT (transitions from AT to conduction band and conduction band to TDDT). For the proposed IMTS model, the transport of carriers during heating can be described by the following TL kinetic rate equations; $[24], 38-41]$.

$$\frac{dn}{dt} = -sn \exp\left(-\frac{E}{kT}\right) + (N-n)n_c A_n, \tag{4.1.1}$$

$$\frac{dm}{dt} = (M-m)n_c A_m, \tag{4.1.2}$$

$$\frac{dn_h}{dt} = \frac{dn}{dt} + \frac{dm}{dt} + \frac{dn_c}{dt}, \tag{4.1.3}$$

$$\frac{dn_c}{dt} = -\frac{dn}{dt} - \frac{dm}{dt} - n_c n_h A_h, \tag{4.1.4}$$

$$I(t) = -\frac{dn_h}{dt} = n_c n_h A_h, \tag{4.1.5}$$

where I is the intensity of the glow-curve; N and M $(cm^{-3})$are the total concentrations of the active and TDDT electron traps; $n(t)$, and $m(t)$ (cm^{-3}) are the corresponding instantaneous concentrations of filled traps, n_c (cm^{-3}) is the instantaneous concentration of electrons in the conduction band, n_h (cm^{-3}) is the concentration of carriers in the recombination centers, A_n is a capture coefficient(trapping or retrapping in the context of thermoluminescence) of a trap for free electron capture, $A_n = \sigma_n v$ where σ_n is the electron capture cross section for the trap and v is the free electron velocity which is about $10^7 cms^{-1}$), and A_m is capture coefficient of the thermally disconnected deep trap (TDDT) for free electron capture, $A_m = \sigma_m v$ where σ_m is the electron capture cross section for the TDDT and v is the same as before. Thus units of A_m is also(cm^3/s), A_h in (cm^3/s) is recombination coefficient of a free electron $A_h = \sigma_h v$ where σ_h is the cross section (cm^2) of the recombination centre for electron capture and E (eV) is the activation energy of the active traps, s (s^{-1}) is the frequency factors for these traps, and k (eV/K) is the Boltzmann constant. The initial concentrations of the dosometric and competitor traps at time $t = 0$ are represented by n_o and m_o, respectively. Moreover, we assume a linear heating rate given by

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

where $T(K)$ is the temperature of the sample at a time t, $\beta(Ks^{-1})$ is the heating rate, $t(s)$ is the time and T_o is the temperature at $t = 0$. In addition to this, the concentration of holes n_h in the recombination center (RC) at any time must be equal to the total instantaneous concentration of electrons due to the conservation of charge in the crystal.

$$n_h = n + m + n_c. \tag{4.1.7}$$

The above rate equations describing the traffic of electrons during the linear heating process, are coupled first-order nonlinear differential equations, which unfortunately cannot

be solved in close form. The development of analytical expressions for the TL intensity as a function of temperature requires simplifying assumptions, with the most important one being the quasi-equilibrium QE (qualitative in nature), very nearly or almost conditions. For the analytical models of thermoluminescence namely the first-order kinetics model of Randall and Wilkins, second-order kinetics models of Garlick and Gibson, general-order kinetics model of May and Partrige, and mixed-order kinetics model of Visocekas, the recombination plus retrapping rate during heating are assumed to be equal to the thermal stimulation rate which means that the excited charge carriers during heating to read the TL are assumed to instantly relax either into the available recombination centers (RC) or into the vacant traps. This descries that the equilibrium of the excited state (conduction band, assuming that the traps are of electron type) existing before the start of the heating the sample to read its TL remains undisturbed which is described mathematically by equation $dn_c/dt = 0$ where n_c is the concentration of the electrons in the conduction band. The charge carriers have a finite life time in the excited state in real cases. The excited carriers therefore tend to stay in that state for a time length which depends on the life time of the given state. Thus there may take place some build up of the carriers in the excited state. However if this build up is negligible in comparison to the population n of the active traps at all temperatures T during heating the equilibrium of the excited state is assumed to be undisturbed for all practical purposes. This is called the quasi-equilibrium (QE) approximation. For the simple one trap-one recombination centre (OTOR) model, mathematically the QE approximation is expressed as $n_c \ll n$ and $dn_c/dt \ll dn/dt$ or $dn_c/dt \approx 0$. Analytical expressions are thus very important in understanding the TL theory. Different authors have therefore attempted to fix the criteria that is, the extent to which the disequilibrium may be allowed so that the analytical expressions may be assumed valid for all practical purposes [1, 5, 12]. Essentially this means to determine how small the smaller of the quantity should be in comparison to its greater counterpart in the above inequalities. To understand the QE approximations we need to describe the transport of the released charge carriers from the traps to the RC during the

heating in terms of the rate equations in an exact manner for chosen physical models. QE approximations may then be applied to the rate equations to arrive at the analytical expressions. For our investigation of physical models of TL using the rate equations, the QE approximations used (interactive multi trap system (IMTS) model) are;

$$n_c \ll (n+m), \tag{4.1.8}$$

$$|dn_c/dt| \ll |-dn/dt - dm/dt|, \tag{4.1.9}$$

where the meaning of various terms in these inequalities is already given before. The coupled nonlinear differential equations of varying coefficients describes above are the rate equations determining the TL process and unsolvable analytically in general cases. The value of coefficients A_m, A_n and A_h range is believed to be as low as $10^{-10}\ cm^3 s^{-1}$ and as high as $10^{-5}\ cm^3 s^{-1}$ [32],[41 − 43].

For the numerical simulations of our investigation, the following numerical values were (to clearly understand the glow curves of each QDs) used for the parameters; $A_n = 10^{-9}\ cm^3/s$, $A_m = 10^{-9}\ cm^3/s$, $N = M = 10^{16}\ cm^{-3}$, $n_0 = 2 \times 10^{14}\ cm^{-3}$, $m_0 = 2 \times 10^{14}\ cm^{-3}$, $\beta = 1\ K/s$, $E = 0.75\ eV$, $s = 10^8\ s^{-1}$, and $A_h = (3.5,\ 2.0,\ 0.45,\ 0.02) \times 10^{-8}\ cm^3/s$ and are used to plot the graphs of n versus T, n_c versus T, m versus T, $Intensity$ versus T; all in the temperature range $T = 0 - 250\ K$. The size-dependent capture coefficient, A_h, shown in table is used for QDs of radii 1.5, 2.0, 2.5 , 3.0 nm. In this model, the retrapping terms with the coefficients A_i is taken into account. It considerably complicates the system of Eqs. 4.1.1 - 4.1.5 that becomes nonlinear and cannot be solved analytically in general case. We solved this system of equations numerically with the help of Mathematica 9 software with the given parameters . It should also known that the confinement must increase the radiative recombination probability. In the numerical simulations we have calculated the TL glow curves for selected sets of parameters using the IMTS model in the rate equations. Calculations were carried out numerically. Figs. 4.2 - 4.6 shows the glow curves for different parametric combinations to examine the

Table 4.1: Size dependent electron-hole recombination coefficient A_h of silicon quantum dots of radii 1.5, 2.0, 2.5 , 3.0 nm. Note $n_h = n_0 = 2 \times 10^{14}\ cm^{-3}$[12].

No.	Radii of QDs (nm)	*Radiative recombination rate*, $\tau_h^{-1}\ (s^{-1})$	$A_h = (\tau_h n_h)^{-1}$
1	1.5	7.0×10^6	3.5×10^{-8}
2	2.0	3.0×10^6	1.5×10^{-8}
3	2.5	9.0×10^5	4.5×10^{-9}
4	3.0	4.0×10^5	2.0×10^{-9}

changes in peak temperature T_m and the peak shape factor δ/ω due to the changes in QDs size values. The values of the parameter A_h for the QDs size are changed, to examine the effect of these changes. The initial concentrations n_0 and m_0 of the ATs and the TDDTs are arrived at by assuming that the traps fill with dose according to the saturating exponential function $[42 - 52]$ in which the filling rate constants for ATs (i.e, those traps which are getting thermally excited at a given temperature during recording of TL glow) and the TDDTs are assumed to be proportional to A_n and A_m, respectively.

Figure. 4.2 depicts the variation of trapped electrons $n(T)$ in the trap AT as a function of temperature for different size of QDs of diameter $3nm - 6nm$. The concentration of electrons in the trap is initially constant up to a temperature equal to $79.53\ ^0C$ and concentration $n(T)$ of approximately about $1.973\ \times 10^{14}\ cm^{-3}$, which indicates that the trap is not yet activated. There after concentration of electrons $n(T)$ in the AT decreases as the temperature increases until it is completely emptied just above $181.8\ ^0C$ and $n(T)$ of $6.796\ \times 10^{11}\ cm^{-3}$. In addition to this, it is observed that concentration of electrons is almost independent of the size of the QDs. Moreover, the value of the ratio A_n/A_h of the QDs size, i.e. the recombination probability coefficient A_h are $.03 \times A_n$, $0.06 \times A_n$, $0.22 \times A_n$ and $0.50 \times A_n$ larger than the retrapping probability coefficient A_n respectively for the QDs, one would expect that first-order kinetics will dominate the kinetic process for the given QDs sizes. The calculated TL glow curve has indeed the characteristic shape for first-order peaks.

Figure 4.3 shows the concentrations of electrons in the TDDT as a function of temperature for different of QDs size. The figure shows that for all the QDs size, the instantaneous

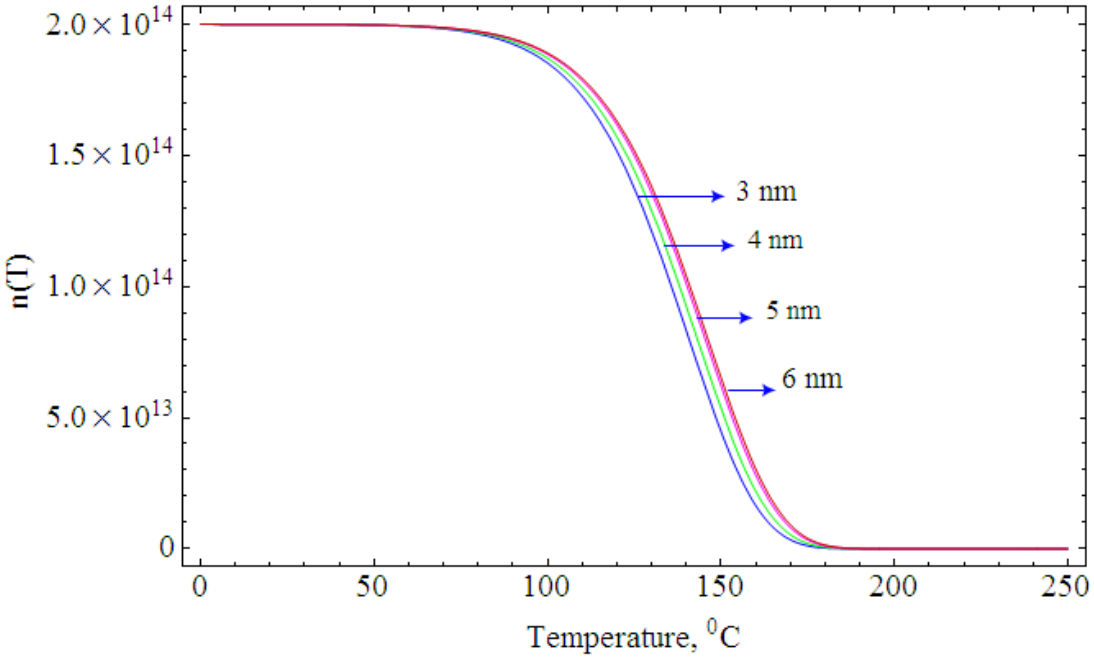

Figure 4.2: The variation of trapped electrons in the trap AT as a function of temperature for different size of QDs of diameter $3nm - 6nm$. The parameters used are; $E = 0.75\ eV$, $s = 10^8\ s^{-1}$, $A_n = A_m = 10^{-9}\ cm^3 s^{-1}$, $A_h = (3.5,\ 1.5,\ 0.45,\ 0.02)\ \times 10^{-8}\ cm^3 s^{-1}$, $N = M = 10^{16}\ cm^{-3}$, $n_o = m_o = 2\ \times 10^{14}\ cm^{-3}$, $\beta = 1Ks^{-1}$.

concentration of electrons $m(T)$ in the TDDT electron traps increases with an increase in temperature until about $180.2\ ^0C$ and concentration $m(T)$ of $3.852\ \times 10^{14}\ cm^{-3}$ and then reaches saturation values almost just after about $180.2\ ^0C$ for each QDs size, shortly after the end of the TL glow curve. The temperature $180.2\ ^0C$ at which $m(T)$ becomes saturated is also nearly the same as to the value where the TL glow curves terminates. Moreover, the saturation values are seen to increase with an increase in the size of QDs. It can be explained in terms of the difference in the recombination probability coefficient, $A_h = (\tau_h n_h)^{-1}$, that means as the the size of QDs increases, the recombination probability coefficient decreases which in turn means lesser number of electrons from active electron trap reaching the RC and producing TL emission instead many more electrons are more likely to be retrapped into the TDDTs before reaching the recombination centre, RC.

Figure. 4.4 shows the variation of concentrations of electrons $n_c(T)$ in the conduction

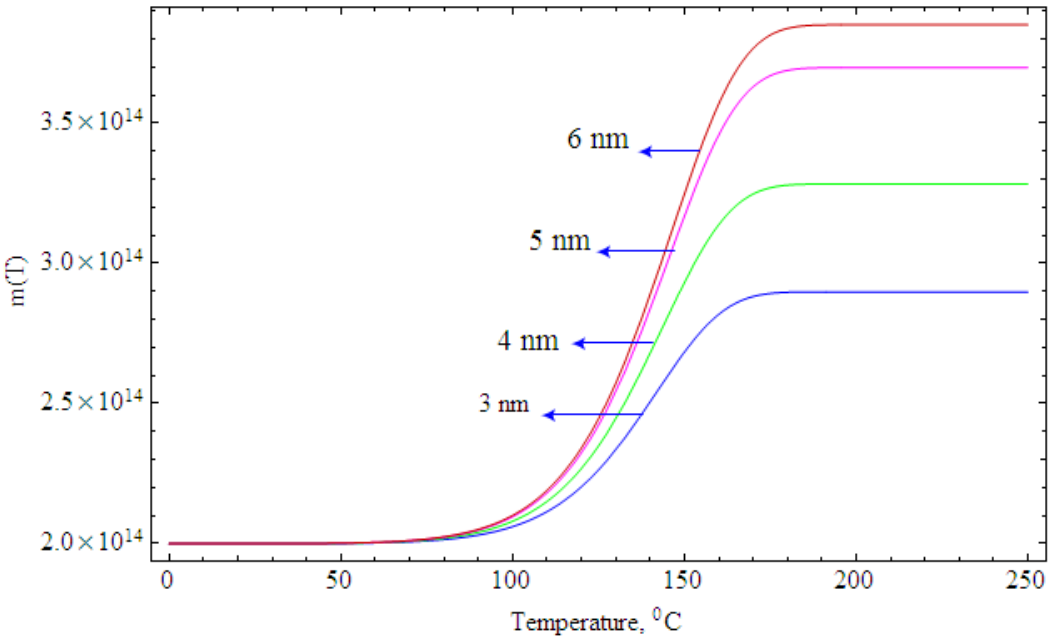

Figure 4.3: The concentration of trapped electrons in the thermally disconnected deep trap (TDDT)as a function of temperature for quantum dot sizes. The parameters used are the same as in Fig 4.2.

band as a function of temperature for different size of QDs of diameter $3\ nm - 6\ nm$. It is observed from this that as the quantum dot size increase, concentrations of electrons $n_c(T)$ also increase. This can be best explained that the recombination lifetime τ_{rec}, of IMTS model Eq. 4.1.10 , which is the mean time spent of the charge carriers (electrons) in the conduction band is larger for the smaller QDs of diameter $3\ nm$. The value of τ_{rec} is simply the inverse of the recombination rate (radiative plus non-radiative) of the free carriers in the conduction band. It mean that free electrons in the conduction band spend more time before recombining with holes in the recombination centre RCs in QDs with smaller size of diameter $3\ nm$ than with larger size of diameter $6\ nm$. The recombination rate gives the rate of the clearing off the trapped charge carriers from the traps. Retrapping transitions are not included in the clearing off process, because the retrapped charges are thrown back into the conduction band during the heating. In other words, the recombination transition coefficient A_h for the electrons in the conduction band to recombine with holes

in the luminescent centres and hence small A_h (equivalently the larger quantum dot size QDs) means the slow rate of recombination with holes as the electron spend more time in the conduction band given by;

$$\tau_{rec} = \frac{1}{[\{n(T) + m(T)\}A_h + \{M - m(T)\}A_m]} \tag{4.1.10}$$

where the term $\{M-m(T)\}A_m$ in the denominator represents the non-radiative relaxation probability. Low value of τ_{rec} is achieved if the values of $n(T)$, $m(T)$, M, A_h, and A_m are high. For the traps could be emptied efficiently for the glow peaks to be observed, τ_{rec} should be sufficiently smaller than the time taken in recording a glow peak, $T_R = (T_f - T_0)/\beta$ where T_f and T_0 are the temperature at the end of the glow peak and at the start of heating and β is the heating rate.

We can also understand that the $n_c(T)$ and TL(T) maxima occur nearly at the same temperature for each QDs and the corresponding T_m for each is $142.2\ ^0C$, $144.0\ ^0C$, $145.5\ ^0C$ and $146.4\ ^0C$ respectively for QDs of diameter $(3, 4, 5, 6)nm$ indicating that there is an approximately a slight change in the TL peaks temperature of $\Delta T_m = 2\ ^0C$ between consecutive QDs and are shifted with respect to each other.

It is worthwhile to note that unlike experimental techniques in which only the TL glow curves are generated, the numerical(theoretical) method enables us to observe the dependency of concentration of carriers in the system on the variations of quantum dot size QDs and temperature (T).

.

From Fig. 4.5 one can also observe how the intensity of the TL signal vary as a function of temperature. The figure shows that the thermoluminescence intensity of silicon quantum dots as function of temperature decrease as the quantum dots sizes increase or equivalently A_h decrease. The enhancement of the TL signal with a decrease in QDs size may be explained with the fact that the intensity of TL emission from quantum dots is enhanced with increased quantum confinement (decrease in the size of QDs) since the confinement effect causes an increase in the number of surface states thereby resulting to more holes and electrons to be accessible for the TL recombination, and the wave functions

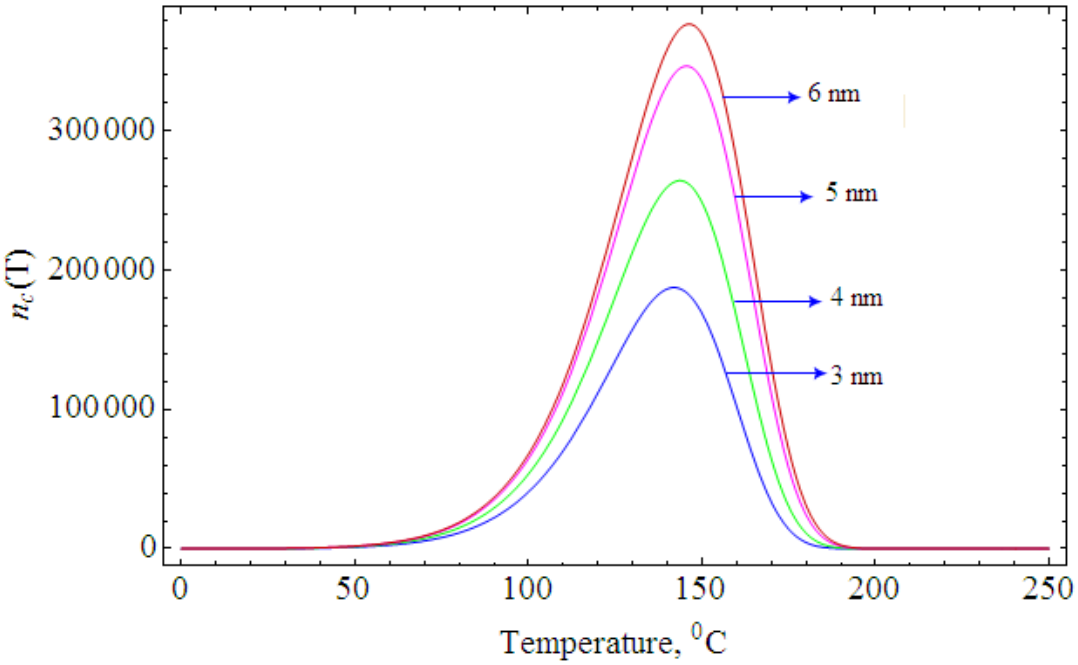

Figure 4.4: The instantaneous concentration of free electrons in the conduction band $n_c(T)$ as function of temperature for different size of QDs. The parameters used are the same as in Fig 4.2.

of the electrons and holes in the QDs are overlapped effectively, which in turn results in the increase of their radiative recombination rate, τ_h, (or equivalently with a decrease of the recombination probability coefficient, $A_h = (\tau_h n_h)^{-1}$ [24]. In other words the intensity of the TL glow curves as a function of temperature for the theoretical values of irradiation dose $n_0/N = m_0/M = 0.02$, $A_n = A_m = 10^{-9}\ cm^3 s^{-1}$, $A_n/A_h = 0.3,\ 0.7,\ 2.2,\ 5.0$ and for quantum dot sizes of $1.5,\ 2.0,\ 2.5,\ 3.0\ nm$, i.e., $A_h = (3.5,\ 1.5,\ 0.45,\ 0.02) \times 10^{-8}\ cm^3 s^{-1}$ it is observed that when the quantum dots sizes increase, the intensity of TL emission decrease. The maximum temperature of the TL glow curves increases with an increase of the quantum dot size with the observed maximum shift between consecutive QDs being $\Delta T_m = 2\ ^0C$ when the radii of the QDs increases. Specifically, comparison of the intensity from TL versus T curve of Fig. 4.5 shows $2.184 \times 10^{12}\ cm^{-3} s^{-1}$ for the $3.0\ nm$ QD relative to $2.95 \times 10^{11}\ cm^{-3} s^{-1}$ that of the $1.5\ nm$ QDs , results in an increase of about 13.5 % other values are tabulated in table 4.2 shown.

Furthermore, the geometrical (shape factors) properties of glow curves or peaks as well as the relevant parameters such as peak temperature at the maximum TL intensity (T_m), temperatures T_1 and T_2 on either side of T_m corresponding to the half-maximum intensity $I_m/2$, $\tau = T_m - T_1$ is the half-width at the low temperature side of the peak, $\delta = T_2 - T_m$ is the half-width toward the fall-off side of the glow peak, $\omega = T_2 - T_1$ is the total half-width $\mu = \delta/\omega$ is the geometrical shape or symmetry factor are determined as shown in Table 4.2. The widths of the glow curve almost remains constant which is independent of the sizes of the quantum dots, i.e, $\omega = T_2 - T_1 \approx 46\ ^0C$. For all the quantum dot sizes, thermoluminescence glow curves have asymmetrical shapes and size corresponding to characteristics of first-order 'looking' glow curve with $\mu_g \rightarrow 0.42$ and order of kinetics $b \rightarrow 1$; which is mainly attributed to the larger number of electrons in the TDDT traps [53]. Also comparison of glow curves of Figs. 4.4 and 4.5 shows that the simulated TL glow curves has a very similar shape and the same peak temperature T_m as that of concentration of electrons in the conduction band.

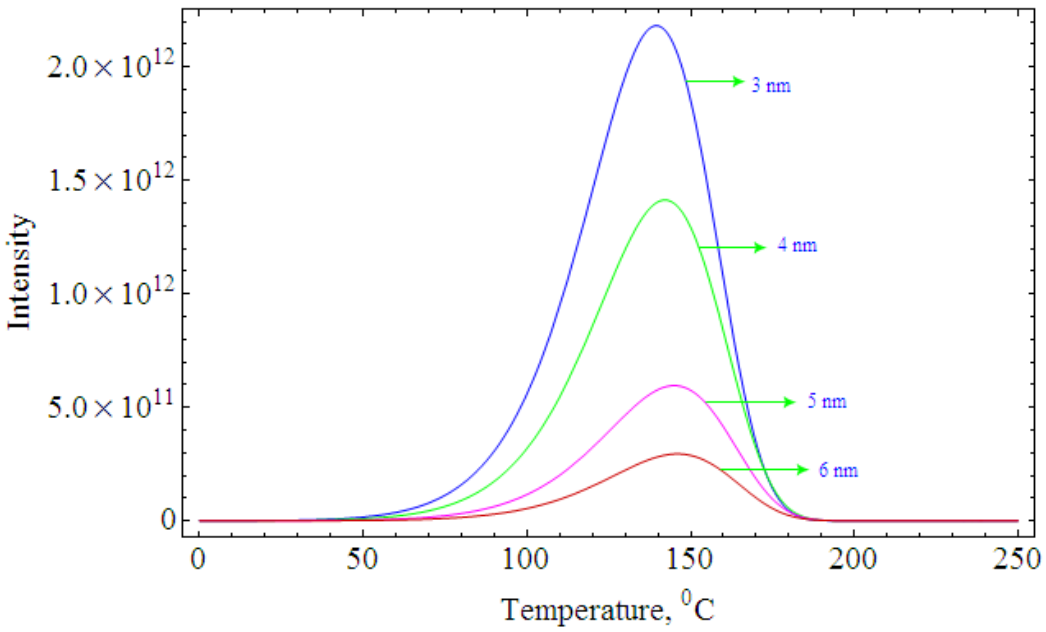

Figure 4.5: The thermoluminescence intensity of silicon quantum dots as function of temperature using IMTS model. The parameters used are the same as in Fig 4.2.

Table 4.2: The values of the geometrical or shape factors; peak temperature T_m, T_1, T_2, symmetry factor μ, δ, ω, γ, for each computed glow curve of different QDs size (IMTS model).

Radii (nm)	$T_m\ (K)$	$T_1\ (K)$	$T_2\ (K)$	$\delta\ (K)$	$\tau\ (K)$	$\omega\ (K)$	$\mu = \delta/\omega$	$\gamma = \delta/\tau$
1.5	412.5	386.0	432.2	19.7	26.5	46.2	0.426	0.74
2.0	415.3	388.0	435.0	19.7	27.3	47.0	0.419	0.72
2.5	417.3	391.6	437.4	20.1	25.7	45.8	0.438	0.78
3.0	418.3	392.9	438.6	20.3	25.4	45.7	0.444	0.79

The geometrical (shape) factor($\mu = \mu_g = \delta/\omega$) for each QDs is calculated for 1.5 nm dot size as a sample and for the rest QDs size calculated in the same way are tabulated in the table 4.2) as;

$$\mu = \frac{\delta}{\omega} = \frac{T_2 - T_m}{T_2 - T_1} = \frac{159.2 - 139.5}{159.2 - 113.0} = 0.4264. \tag{4.1.11}$$

which is nearly the same value as that of first order kinetics, $\mu_g = \mu \rightarrow 0.42$.

Let us now calculate an important parameters of TL glow curves such as activation energy E kinetic order b and frequency factor s using the general peak shape method equation for evaluating the activation energy E is given by Eqs. 3.6.15 - 3.6.20 and tabulated in table 4.3. Chen derived general expressions for evaluating E and it is useful for a broad range of energies ranging between 0.1 eV and 2.0 eV, and for values of the pre-exponential factors between $10^5\ s^{-1}$ and $10^{23}\ s^{-1}$. In addition, Chen's method does not make use of any iterative procedures and does not require knowledge of the kinetic order, which is found by using the symmetry factor μ from the peak shape. By using the different parameters values of energies for each QDs and kinetic order b are summarized in table below where, α represents τ, δ or ω. Let us calculate E_τ, E_ω, E_δ for $3nm$ diameter dot as a sample and record for other QDs accordingly;

$$C_\omega = 2.52 + 10.2(0.43 - 0.42) = 2.622, \tag{4.1.12}$$

$$C_\tau = 1.510 + 3.0(0.43 - 0.42) = 1.54, \tag{4.1.13}$$

Table 4.3: Calculated values of activation energies corresponding to E_τ, E_ω, E_δ and kinetic order (b) and frequency factors s (for IMTS and OTOR models) of each silicon quantum dots.

No.	R(nm)	E_τ (eV)	$E_\omega(eV)$	$E_\delta(eV)$	b	$s(s^{-1}), IMTS$	$s(s^{-1}), OTOR$
1	1.5	0.736	0.761	0.781	1.1	1.03×10^8	6.09×10^8
2	2.0	0.710	0.725	0.736	1.0	3.04×10^7	6.47×10^8
3	2.5	0.783	0.787	0.783	1.1	1.67×10^8	2.96×10^8
4	3.0	0.812	0.827	0.833	1.2	5.05×10^8	1.65×10^8

$$b_\tau = 1.58 + 4.2(0.43 - 0.42) = 1.622, \tag{4.1.14}$$

$$c_\delta = 0.976 + 7.3(0.43 - 0.42) = 1.049, \tag{4.1.15}$$

$$b_\delta = 0, \qquad b_\omega = 1. \tag{4.1.16}$$

$$E_\delta = 1.049\left(\frac{8.617 \ \times 10^{-5} \ \times 412.5^2}{19.7}\right) - 0 = 0.781 \ eV. \tag{4.1.17}$$

similarly, $E_\tau = 0.736 \ eV$ and $E_\omega = 0.761 \ eV$. From the calculated values of corresponding energies of each QDs, we can observe that the values are nearly close (specifically that of E_ω) to the theoretical value 0.750 eV. The frequency factor s according to Chen ranges between 10^5 and 10^{23} s^{-1}, thus using values $E_\omega = (0.761, \ 0.725, \ 0.787, \ 0.827) \ eV$ for each QDs, we calculated by Eqs. 4.1.18 and 4.1.19 that the value of s fall within the range and are close to the theoretical value 10^8 s^{-1} in both simulated models [5].

$$s = \frac{\beta E}{kT_m^2} \ \exp\left(\frac{E}{kT_m}\right), \qquad \text{for first order and} \tag{4.1.18}$$

$$s = \frac{\beta E}{kT_m^2\left(1 + \frac{2kT_m}{E}\right)} \ \exp\left(\frac{E}{kT_m}\right), \qquad \text{for second order} \tag{4.1.19}$$

Next we considered the case for which the TDDT trap is not present by setting $M = m_o = 0$ or equivalently the capture coefficient of the thermally disconnected deep trap

Table 4.4: The values of the geometrical or shape factors; peak temperature T_m, T_1, T_2, symmetry factor μ, δ, ω, γ, *kinetic order*, (b) for each computed glow curve of different QDs size (OTOR model).

R(nm)	T_m (K)	T_1 (K)	T_2 (K)	δ (K)	τ (K)	ω (K)	$\mu = \delta/\omega$	$\gamma = \delta/\tau$	b
1.5	422.0	393.0	453.0	31.0	29.0	60.0	0.517	1.06	1.97
2.0	433.0	401.0	468.0	35.0	32.0	67.0	0.522	1.09	2.02
2.5	453.8	420.0	492.6	38.8	33.8	72.6	0.534	1.15	2.14
3.0	470.4	432.9	511.0	40.6	37.5	78.1	0.519	1.08	1.99

(TDDT) for free electron capture $A_m = 0$ in the coupled nonlinear differential equations of Eqs. $(4.1.1 - 4.1.5)$, in which the IMTS model reduces to OTOR model as a function of temperature for the same QDs sizes that are used for the IMTS model. It is observed that the TL intensity is found to increase with a decrease of the QDs sizes (which is observed from Fig. 4.6 that the T_m for decreasing QDs are; 197 ^0C, 180.3 ^0C, 160 ^0C, 149.3 ^0C at a concentrations of; 2.16×10^{12} $cm^{-3}s^{-1}$, 2.34×10^{12} $cm^{-3}s^{-1}$, 2.66×10^{12} $cm^{-3}s^{-1}$, 2.93×10^{12} $cm^{-3}s^{-1}$ respectively, while the peak temperature T_m shifts towards the higher values with an increase in QDs size as shown.

In addition to these, the shape properties of the glow curves for OTOR model are determined and shown in Table. 4.4. It is seen that the widths ω (i.e, 60, 67, 72.6, 78.1) (K) for increasing QDs size at half-maxima of the glow curves become broader and broader with an increase in QDs size. Also unlike the results that are obtained using IMTS model, the TL glow curves possess almost symmetrical shapes indicating that the OTOR model results to second- order 'looking' glow peaks with $\mu_g = \mu \rightarrow 0.52$ and order of kinetics $b \rightarrow 2$. This is due to the fact that in the absence of TDDT traps, the occurrence of second order kinetics requires that the electron trap (in our case the ratio $n_o/N = 2 \times 10^{14}$ $cm^{-3}/1 \times 10^{16}$ $cm^{-3} = 0.02$) is far from being saturated [54].

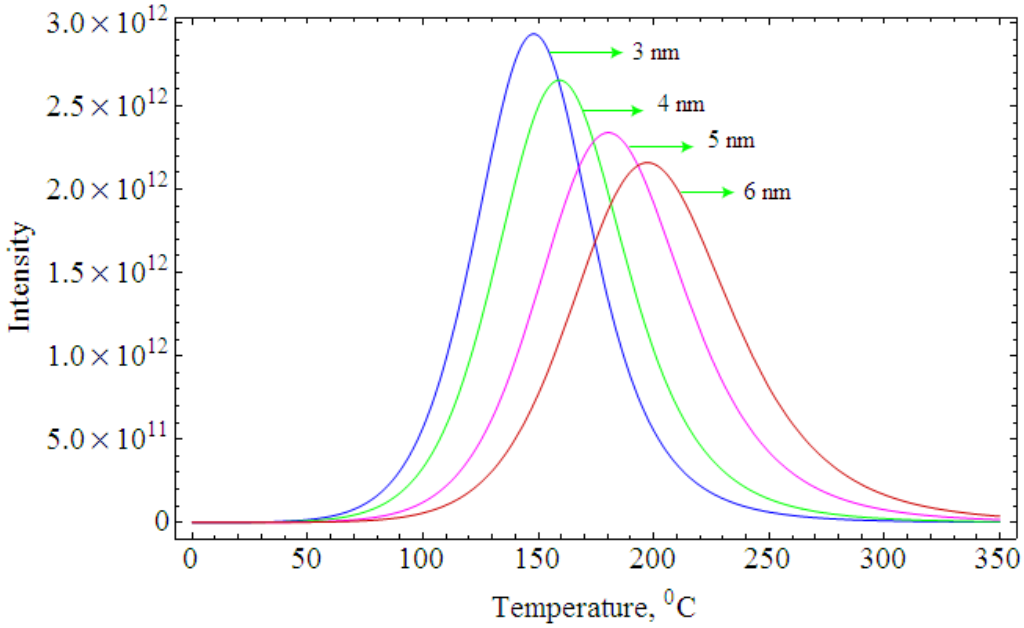

Figure 4.6: The thermoluminescence intensity of silicon quantum dots as function of temperature, using OTOR model. The parameters used are the same as in Fig 4.2, but in this case $M = m_o = 0$.

Chapter 5

Conclusions

In this thesis, the numerical results of thermoluminescence intensity of silicon quantum dots of radii $1.5\ nm,\ 2\ nm,\ 2.5\ nm,\ 3\ nm$ using the Interactive Multi Traps system Model (IMTS) are studied and the corresponding variations of $n(T)$, $n_c(T)$, $m(T)$, and $TL(T)$ for both IMTS and OTOR models as a function of temperature of each dot size are compared. Employing the IMTS TL kinetic model, we investigated the TL glow curves and determine relevant parameters of interest of TL emission from amorphous silicon quantum dots having different sizes. The size effect on TL signal is taken into account through the size dependent recombination probability coefficient, (A_h). We find that as the quantum dots sizes increase or equivalently A_h decrease, the intensity of the thermoluminescence signal is enhanced. Furthermore, for the same QDs size, the TL intensity as a function of the QDs size simulated using one trap- one recombination centre (OTOR) model, i.e, by setting both total concentration of thermally disconnected deep traps (TDDT) and Concentration of filled TDDT at the beginning of heating to read the TL equal to zero $(i.e, M = m_o = 0)$ in the IMTS kinetic rate equations. Similar to that obtained using the IMTS model, the intensity of the TL emission is found to increase with a decrease in the size of the quantum dots. These enhancements of the the intensity of TL signal with a decrease in QDs sizes may be attributed to the quantum confinement effect in a non-structured materials. Furthermore, our analysis show that irrespective of the presence of retrapping (i) the IMTS model leads to first order looking glow curves with

$\mu_g = \mu \rightarrow 0.42$ and order of kinetics $b \rightarrow 1$, while the glow curves simulated using the OTOR model resembles a second order kinetics with $\mu_g = \mu \rightarrow 0.52$ and order of kinetics $b \rightarrow 2$ and (ii) for OTOR model, the peak temperature T_m shifts towards the higher values with an increase in QDs sizes, whereas it is almost independent of size for IMTS model. In addition, the instantaneous concentration of carriers in the electron traps, in the conduction band and RC are determined. The results show that the concentration of electrons in the AT decreases as the temperature increases. In addition TL T_m of each QDs occur nearly at the same temperature and the the shape factor for each QDs is also maintains approximately that of first order kinetics (0.42). In similar manner the concentrations of trapped electrons in the TDDTs as a function of temperature for the QDs sizes increases with temperature with small temperature difference in each sizes and reaches saturation after short period of time with increasing QDs sizes. We also find that, the concentration of electrons in the AT decreases as the temperature increases, while the instantaneous concentration of electrons in the conduction band has a very similar shape to the measured TL glow curve. In addition TL T_m of each QDs occur nearly at the same temperature and the concentration of electrons in the TDDT increases with temperature in each QDs, and reaches saturation after $172.8\ ^0C$, $177.5\ ^0C$, $180.5\ ^0C$ and $183.1\ ^0C$ respectively for the increasing QDs size. Moreover, we find the variation of concentrations of electrons $n_c(T)$ in the conduction band as a function of temperature for different size of QDs of diameter $3\ nm - 6\ nm$ and it is observed from this that as the quantum dot size increase, concentrations of electrons $n_c(T)$ also increase due to the recombination lifetime τ_{rec} of the charge carriers (electrons) of the QDs in the conduction band (more time is spent for small quantum dot in the CB). Furthermore, when the quantum dots sizes increase or equivalently A_h decrease, the intensity of the thermoluminescence glow curves decrease. Specifically, comparison of the intensity of each dots are at nearly no temperature difference and the shape factor for each QDs is nearly the same value as that of FO kinetics. The $n_c(T)$ and TL(T) maxima occur nearly at the same temperature for each QDs and the corresponding T_m for each is $142.2\ ^0C$, $144.0\ ^0C$, $145.5\ ^0C$ and

146.4 ^0C respectively indicating that there is an approximately a slight change in the TL peaks temperature of $\Delta T_m =$ 2 ^0C between QDs and are shifted with respect to each other. Similarly for OTOR model, the corresponding T_m for decreasing QDs are; 197 ^0C, 180.3 ^0C, 160 ^0C, 149.3 ^0C with temperature difference of nearly $\Delta T_m =$ 12 ^0C - $\Delta T_m =$ 20 ^0C between each dots. The thermoluminescence intensity of silicon quantum dots as function of temperature decrease as the quantum dots sizes increase or equivalently A_h decrease and the glow curves have almost characteristics of first order kinetics for IMTS model and the intensity of the TL is found to increase with a decrease of the QDs sizes and we observed that the T_m shifts towards the higher values with an increase in QDs size indicating that the glow curves have almost characteristics of second order kinetics for OTOR model. Finally, we believe that the results in this investigation may be used during the design and fabrication of dielectric compounds enriched in different ways with silicon contents for TL applications. Furthermore, it may motivate further theoretical and experimental investigations of the study of the TL phenomena in silicon quantum dots.

Bibliography

[1] S.W.S. McKeever, Thermoluminescence of Solids, Cambridge University, Cambridge (1985).

[2] J.T.Randall and M.H.F. Wilkins, Proc. Roy. Soc., A 184, 366 (1945).

[3] K.Mahesh, P. Weng, C. Furetta, Thermoluminescence In Solids and Its Applications, Ashford, Kent, England, UK. Nuclear Technology Pub. (1989).

[4] C.M. Sunta, E. Okuno, J.F. Lima, E.M.Yoshimura, J. Phys. D Appl. Phys., 27, 2636 (1994).

[5] V. Pagonis, G. Kitis and C. Furetta, Numerical and Practical Exercises in Thermoluminecsnce, USA, Springer, (2006).

[6] G.F.J. Garlick and A.F.Gibson, Proc. Phys. Soc., 60, 574 (1948).

[7] C.E. May and J.A. Partridge, J.Chem. Soc., 40, 1880 (1964).

[8] B.M. Ilich, Sov. Phys. Solid State., 21, 1880 (1979).

[9] V. Pagonis and G. Kitis, Radiat. Prot. Dosimetry., 95, 225 (2001).

[10] R. Chen, N. Kristianpoller, Z. Davidson and R. Visocekas, Journal of Luminescence 23, 293 (1981).

[11] R. Chen and Y. Kirsh, Analysis of Thermally Stimulated Processes, Pergamon Oxford (1981).

[12] Vasilis Pagonis and George Kitis, Prevalence of First-Order Kinetics In Thermoluminescence Materials, Phys. Status Solidi B, 1 (2012).

[13] Horowitz, Y.S, Thermoluminescence and Thermoluminescent Dosimetry, Boca Raton, Vol.1 (1984).

[14] Furetta, C., Questions and Answers on Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL), World Scientific Publishing Co. Pte. Ltd. Singapore (2008).

[15] S. Tripathy, R. K. Soni, S.K. Ghoshal and K. P. Jain, Mater. Sci. 24, (2005).

[16] Zhiyong Zhou, Michael L. Steigeward, Richard A. Frienser, and Louis Brus, Phys. Rev. B, 71, (2005).

[17] N. M. Abdul-Ameer, M. C. Abdulrida, Journal of Modern Physics, 2, 1530 (2011).

[18] T. F. Jiang, X. Tong and S. Chu, Self-Interaction-Free Density Functional Theoretical Study of the Electronic Structure of Phy sical Review B, Vol. 63, 1530 (2001).

[19] Y. Alhassid , The Statistical Theory of Quantum Dots," Reviews of Modern Physics, Vol. 72, 895 (2000).

[20] J. S. Williams, R. G. Elliman, H. H. Tan, P. Lever, J. Wong-Leung and C. Jagadish Production and processing of Semiconductor Nanocrystals And Nanostructures for Photonic Applications, Materials Forum, Vol. 26, 74 (200).

[21] Charles Kittle, Introduction to Solid State Physics, Eighth edition, USA (2005).

[22] D. Curie, Luminescence in crystals, John Wiley Sons Inc. New York, (1963).

[23] X. Qin, Y. Ju, S. Bernhard, N. Yao, Mater. Res. Bull, 42, 1440 (2007).

[24] S.W.S. McKeever, Thermoluminescence of Solids, Cambridge Solid State Science Series, Oklahoma State University (1988).

[25] R. Chen, J. ElectrochemSoc. Solid State Sci, 116, 1254 (1969).

[26] M. Karmakar, Indian J. Phys, 84, 529 (2010).

[27] Y. Parganiha, J. Kaur, V. Dubey, D. Chandrakar, N. Suryanarayana, Research Chem. Intermed, 42, 2267 (2015).

[28] E. Pekpak,A. Ylmaz, G. Ozbayoglu, J. Alloy. Compds, 509, 2466 (2011).

[29] Y. Parganiha, J. Kaur, V. Dubey D. Chadrakar, Superlattice. Microst, 77, 152 (2015).

[30] Reuven Chen, J. Phys. D. Appl. Phys, 16, 107 (1983).

[31] R. Chen, N. Kristianpoller, Z. Davidson,R. Visocekas, Lum, 23, 293 (1981).

[32] R. Chen, S.W.S. McKeever, Theory of Thermoluminescence and Related Phenomenon, World Scientific, Singapore (1997).

[33] C.Furetta, Handbook of Thermoluminescence, World Scietific, Singapore (2003).

[34] R. Chen,Y. Kirsh, Analysis of Thermally Stimulated Processes, (Pergamon Press, Oxford (1981).

[35] C. M. Sunta, W. E. Ayta, T. M. Piters, and S. Watanabe, Radiat.Meas, 30, 197 (1999).

[36] C. M. Sunta, W. E. Ayta, J. F. D. Chubasi,and S. Watanabe, Radiat. Meas, 35, 47 (2002).

[37] N. G. Debelo, Lat. Am. J. Phys. Educ, 6, 327 (2012).

[38] Pagonis, V. Chen, R. Lawless, J. L, Nonmonotonic Dose Dependence of OSL Intensity Due To Competition During Irradiation and Readout, Radiation Measurements, 41, 903 (2006).

[39] C.M. Sunta, W.E.F. Ayta, J.F.D. Chubaci, S. Watanabe, J. Phys. D Appl. Phys, 34, 2690 (2001).

[40] M. Kumar, R.K. Kher, C.M. Sunta, J. Phys. D Appl. Phys, 39, 2670 (2006).

[41] R. Chen and V. Pagonis, Thermally and Optically Stimulated Luminescence, A Simulation Approach John Wiley and Sons, Chichester (2011).

[42] G. Adamiec, M. Gracia-Talavera, R. Bailey, and P. Iniguez de la Torre, Geochronometria, 23, 9 (2004).

[43] M. Akselrod, V.S. Kortov, D.J. Kravetsky, V.I. Gotlib, Radiat. Prot. Dosim, 33, 119 (1990).

[44] W. Hoogenstraaten, Philips Res. Rep, 13, 515 (1958).

[45] M. Akselrod, N.A. Larsen, V. Whitley, S.W.S. McKeever, J. Appl. Phys, 84, 3364 (1998).

[46] M. Akselrod, V.S. Kortov, D.J. Kravetsky, V.I. Gotlib, Radiat. Prot. Dosim, 32, 15 (1990).

[47] C.M. Sunta, E. Okuno, J.F. Lima, E.M. Yoshimura,J. Phys. D Appl. Phys, 27, 2636 (1994).

[48] R. Chen, D. Lo, J. L. Lawless, Radiat. Prot. Dosim, 119, 33 (2006).

[49] R. Tousey, K. Watanabe, D. Purcell, Phys. Rev, 83, 792 (1951).

[50] Y. Parganiha, J. Kaur, V. Dubey D. Chadrakar, Superlattice. Microst, 77, 152 (2015).

[51] R. Tousey, K. Watanabe, D. Purcell, Phys. Rev, 83, 792 (1951).

[52] K. Watanabe, M.K. Slattery, J. Opt. Soc. Amer, 16, 398 (1928).

[53] K. Ankama Rao, Sk.p. Niyaz, N.V. Poornachandra Rao and K.V.R. Murthy, Archives of Physics Research, 2(4), 89 (2001).

[54] M. Karmakar, S Bhattacharyya, A Sarkar, P S Mazumdar and S.D Singh, Radiation Protection Dosimetry, 175, 4, 493 (2017).