ANALYSIS OF THERMOLUMINESCENCE GLOW CURVES FOR FIRST-ORDER KINETICS

By

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

ADDIS ABABA, ETHIOPIA
APRIL 2019

ADDIS ABABA UNIVERSITY
DEPARTMENT OF PHYSICS

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Dated: April 2019

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Date: **April 2019**

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Title: **Analysis of Thermoluminescence Glow Curves for First-Order Kinetics**

Department: **Physics**

Degree: **M.Sc.** Convocation: **April** Year: **2019**

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Abstract

We have analyzed thermoluminescence glow curves the first-order kinetics using the method based on various heating rate. Employing this method, thermoluminescence intensity versus temperature of the glow curves of first order kinetics was plotted for the different values of heating rate, β. by using MATHEMATICA and SPSS softwares, we analyzed these glow curves and discussed the results through evaluating numerical and graphically the activation energies and the frequency factors from glow curves based on the method of various heating rates. For first-order peaks, the method of finding the glow parameters by measuring the shift of the maximum temperature with changing heating rate is studied. In addition, the instantaneous concentration of electrons in the electron traps and the conduction band are simulated.

Acknowledgements

First of all I would like to thank the almighty God, my strength, power and leading me to this position.

My endless heart feel thankful goes to my advisor Dr. Belayneh Mesfin for his marvelous and remarkable advise, suggestions and constant support in academic and social affairs. He is always in my heart in gravitating me to study and love condensed matter physics. I Wish him success, peace and grace throughout his life.

Next I thank my brother, Sintayehu Abi for devoting his valuable time to assist me in different way, like by showing direction to do this project and how to do this project and how to use spss soft ware for different events and my elder brother, Abewa Getenet for motivating and strengthening me to carry out this project.

Also, I would like express my sincere thanks to Department of physics of the Addis Ababa university for facilitating conditions require for my MSc study.

Last but not least, I would also extend my sincere thanks to my all family, for their moral support.

Alemu Alemayehu
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April 2019

Chapter 1

Introduction

TL is a branch of much wider subject called *luminescence* . A cursory overview of luminescence phenomena may, therefore, be useful before taking up the study of the various aspects of TL in detail. Unlike incandescence, luminescence is a cooler and more efficient mechanism of light emission. In luminescence, the light output per unit energy input is much greater than in the case of incandescence. Luminescence is produced by the selective excitation of the atomic or molecular energy levels. Excitation takes the atom or the molecule to a higher energy state. Its fall to ground state results in the emission of light, which is called *luminescence.*

The term *thermoluminescence* (TL) consists of two words: thermo, meaning heat and luminescence, meaning emission of light. These words may appear to mean that the emission of luminescence is caused by heat. This however is not totally true, since heat has only a secondary role in this case. When heat is the primary cause, the emission is called incandescence, for example, the light coming from a hot filament lamp or a burning charcoal. The primary agents for the induction of TL in a material are the ionizing radiations, namely the X-rays, or radiations from radioactive elements to which the sample is pre-exposed. In some materials, ultraviolet light also may excite TL. When the sample is subsequently warmed up, luminescent light is emitted. The act of warming up stimulates the release of the stored energy in the sample due to pre-exposure to the ionizing radiations. The release of this stored energy produces the luminescence. Therefore, some authors have appropriately used an expanded expression for this emission calling it radiation induced thermally stimulated luminescence. Some others have abbreviated it to *radiothermoluminescence* to signify that the TL is induced by the radiations. Some authors call it thermally stimulated luminescence (TSL)[1].

Thermoluminescence (TL) is a luminescence phenomenon of an insulator or semiconductor which can be observed when the solid is thermally stimulated[2]. The essential conditions are necessary to obtain TL emission are:

- the material must be an insulator or semiconductor,
- heat should be applied to the material to trigger luminescence,
- induction (excitation) of TL by exposure to ionizing radiations,
- the material must have at some time absorbed energy during exposure to radiation, and
- stimulation of TL emission by heating subsequent to exposure.

Thermoluminescence (TL) is the thermally stimulated emission of light following the previous absorption of energy from radiation. The record of light intensity against time or against temperature is called *a glow curve.* After the energy release, the output of the emitted light as a function of temperature is called TL glow curves. Shape of the glow curves is one or more peaks of emitted light and some of them may overlap. Magnitudes and shapes/patterns of the glow curves may change depending on the spectral response of the light sensitive device, different filter usage between the sample and the detector and heating rate. In addition, when the sample is irradiated it has only one shot effect.

Among, The most important parameters are activation energy,E, frequency factor,s, and order of kinetics,b. The thermoluminescence processes is analyzed by an empirical and theoretical method in which a parameter called the first-order of kinetics. When the trapped electrons jump up to the conduction band 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 [3, 4].

The main objective of this study is to characterize the TL glow curves for a various heating rate,β. In particular, we seek to:

- theoretically and numerically analyze the thermoluminescence glow curve of first-order kinetics,
- determine the activation energy,E, and frequency factor,s, with in a various heating linear rate,β, and
- determine the properties of glow curve for irradiation does between the values $n0/N = 0.5$ and $n0/N = 1.0$.

What motivates us to study TL phenomena is because that from TL glow curves different parameters of interest, such as the activation energy, E, frequency factors, s, and other relevant parameters can be using the $MATHEMATICA$ Software and other methods. The project is organized as follows: In Chapter 2, we discussed some basic concepts required for understanding the TL phenomena. In Chapter 3, we presented the mathematical expression of the different TL kinetics order. In Chapter

4, we plot the glow curves using $MATHEMATICA$ and the analysis of the shape of the glow curves for the first - order kinetics; and numerically and graphically determine the activation energy and the frequency factor Finally, the main results are summarized in Chapter 5.

Chapter 2

Theoretical Background

In order to analysis thermoluminescence glow curve of first-order kinetics, we must understand thermoluminescence background. Hence, in this chapter, we briefly discuss the following concepts: Fluorescence and Phosphorescence, Insulator and Semiconductors, Energy band and localized levels, Traps and Recombination centers, Types of Luminescence and finally about the kinetics models of thermoluminescence emission.

2.1 Fluorescence and Phosphorescence

Both $fluorescence$ and *phosphorescence* are type of photoluminescence which involves absorption of energy and excitation of atom to higher energy level followed by emission of electromagnetic radiation(or return to low energy state). In both the emitted photon(light) has lower energy than the absorbed photon and emission occurs at a longer wavelength than the incident light. The major difference is the duration for each process to occur after the initial absorption of light of correct wave length[3].

Many substances continue to luminesce for extended periods even after the exciting energy is cut-off. The delayed emission is generally called *phosphorescence* and emission during the time of excitation is called *fluorescence.* After the absorption of radiation, the emission of light takes place in a characteristic time t and this parameter allows us to sub-classify the process of luminescence, as shown in Fig. 2.1[5]. Conventionally, emissions with decay time shorter than 10^{-8} are referred as fluorescence and those with decay time greater than that are known as phosphorescence[5].

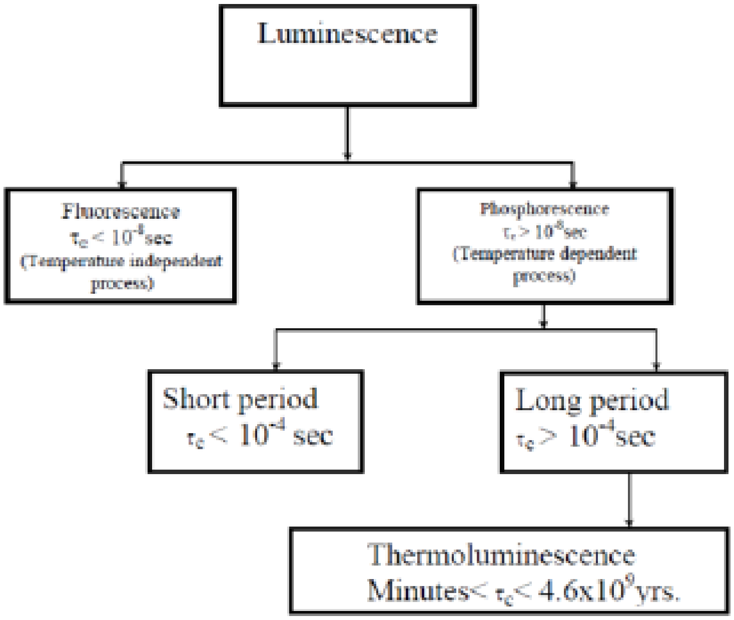

Figure 2.1: The types of luminescence based on the characteristic time t for the emission of light to take place

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Fluorescence takes place simultaneously with the absorption of radiation and stops immediately when the radiation ceases, while phosphorescence continues to be observed after the excitation has been removed. In other words, phosphorescence takes place under the involvement of some metastable state, which is an energy level from which transitions to any lower energy levels are forbidden [5]. Thus, the luminescence that occurs after an electron is brought to a metastable state as a result of the excitation of the system is called phosphorescence. If a system brought to its metastable state is completely unperturbed, then it would remain in such a state for a relatively long period. Absorption transition from the ground state to metastable state is also forbidden.

2.2 Insulators and Semiconductors

Insulators are characterized by a large band gap, so a prohibitively large amount of energy is required to move electrons into the conduction band to form a current, *Semiconductors*, on the other hand, have a small band gap that allows for a meaningful fraction of the valence electrons of the material to move into the conduction band given a certain amount of energy. This property gives them a conductivity between conductors and insulators.

2.3 Energy Bands and Localized Levels

The binding energy of the trapped charge carrier is called the trap depth or the activation energy of the trap[1]. Crystalline solids are found to have energy bands, instead of or in addition to energy levels. Electrons can take on any energy within an unfilled band. At first this appears to be an exception to the requirement for energy levels. However, as shown in band theory, energy bands are actually made up of many discrete energy levels which are too close together to resolve. Within a band the number of levels is of the order of the number of atoms in the crystal, so although electrons are actually restricted to these energies, they appear to be able to take on a continuum of values. The important energy levels in a crystal are the top of the valence band, the bottom of the conduction band, the Fermi level, the vacuum level, and the energy levels of any defect states in the crystal.

A localized states of motion is that in which an electron may be found anywhere within a region of material of linear extent smaller than that of the material [2].

2.4 Traps and Recombination Centers

The deep impurity having energy layer deep in the band gap acts as a recombination center. The aim of such centers, often called *traps*, is to enable fast recombination and short electrons' and holes' lifetime.

Trap is an impurity charged point defect in semiconductor in which minority carrier can be trapped(captured) for a period of time and then released(Thermally "ejected") in to the band form which it originated; this is contrast to a recombination center in which prior the release minority carrier is inihilated by recombination with a captured majority, *recombination center* is an impurity or charged point defected in semiconductor in which a minority carrier is captured and then recombined with subsequently captured majority carrier.

Centers close to the middle of the band gap readily communicate with both bands, since it is easier for a captured electron to recombine with a hole in the valence band than to be emitted into the conduction band. These centers are called *recombination centers*. A more precise way to distinguish between trapping and recombination is given in the following section.

2.4.1 Electron and Hole Traps

There are several transitions possible between any center and other states. All such transitions are described by their corresponding rates. These rates are additive and describe the change in the population of the center. For reasons of detailed balance, there are always pairs of transitions between two states, which must be equal to each other in thermal equilibrium.

The magnitude of transition rates varies from pair to pair over a wide range. For example, thermal excitation of an electron fromthe more distant valence band into an electron trap is much less probable than thermal excitation of a trapped electron into the closer conduction band. In steady state, the total rate of transition from the center must equal the total rate into the center. Usually, one can neglect all transitions compared to the one pair with the highest transition probability. These pairs can now involve different states. Thereby, one can identify different classes of centers according to the predominant types of transitions.

Centers close to the conduction band are identified as $electron-traps$, and centers close to the valence band as $hole-traps$, when these centers communicate predominantly with the adjacent bands[6].

2.4.2 Recombination Process

When the probability of being retrapped is negligible, the glow curve has a narrow peak shape by a rapid recombination process.

Process resulting in annihilation of free charge carrier in semiconductor; reversal of the generation process; typically electron recombining with hole loose energy and moves from the conduction band to valence band[6].

Direct and Indirect Recombinations

In the case of direct recombination an amount of energy will be released with may excited luminescence center(which may coincide with the recombination center).

In real semiconductors, there are some crystal defects and these defects create discrete electronic energy states within the forbidden energy band. Recombination through the defect states which are often referred as trap states is called *indirect recombination.*

Direct recombination is electron in the conduction band releases energy and recombines with hole in the valence band and *indirect recombination* is recombination via centers in the forbidden gap[8].

In recombination and generation processes a certain amount of energy is involved.

In the Shockley-Read-Hall recombination process only two particles are considered, an electron and a hole. The Auger recombination is such a process where three particles are involved; two of them in the process of generation or recombination, and the third that takes or gives some energy. If only Shockley-Read-Hall recombination is assumed four processes are possible. These are:

1. the electron from conduction band can be trapped by an empty trap,
2. a filled trap can emit an electron in the conduction band,
3. an empty trap can emit a hole in the valence band - equivalently, it means that an empty trap will attract an electron from the valence band, and
4. a trap filled with an electron can trap a hole - it means that such a trap will emit an electron in the valence band.

Radiative and Nonradiative Recombinations

Radiative recombination is electron-hole recombination process in which energy is released in the form of electromagnetic radiation; in the case of band-band recombination energy of radiation released corresponds to the band gap of semiconductor, and $non - radiative\ recombination$ is electron-hole recombination process in recombination of electrons and holes which doesnot produce photons, but mostly phonons; i.e not radiation is generated; occurs in semiconductors featuring indirect band gap [8].

The Dexter-Klick-Russell rule states that *radiative recombination* occurs if the optical excitation E_n ends above the crossover E_B, i.e., for relatively weak coupling [5]. Otherwise, the electron will cross over to the lower curve and reach the ground state in a non-radioactive process via multi-phonon emission. Depending on the strength of the coupling, such a crossover for *nonradiative recombination* may or may not require thermal activation; the non-thermal part is accomplished by tunneling to the lower curve.

2.5 Types of Luminescence

Luminescence is the process of emission of electromagnetic radiation from a material upon excitation. Based upon the means of excitation there are various types of luminescence like[11]:

- *Photoluminescence* produced by absorption of light or photons,
- *radioluminescence* produced by the impact of higher energy particles from cosmic rays or radioactive matter, high energy particles from accelerators etc.,
- *electroluminescence* produced by the application of an electric field,
- *mechanoortriboluminescence* produced by the application of mechanical force,
- *cathodoluminescence* produced by cathode rays or electrons,
- *chemiluminescence* produced by chemical process,
- *sonoluminescence* produced by high frequency sound waves or phonons, and
- *bioluminescence* produced by biological processes.

2.6 Model of Thermoluminescence

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 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 in 1945. Instead, if the retrapping dominates, the recombination with the holes is suppressed and the curve has a wide peak explained by Garlick and Gibson in 1948. These two descriptions are called *the first order kinetics and the 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 in 1964. In the second section we will clearly explain these three models i.e., Randall-Wilkins model, Garlick-Gibson model and May- Partridge model. We explain the effect of the activation energy on the glow curves, the effect of the frequency factor on the glow curves and the effect of the initial concentration of filled traps on the glow curves in first-order kinetics using MATHEMATICA for the above mentioned models[3].

2.6.1 One-Trap-One-Recombination Center

The simplest possible model that has been used to describe the process by which materials emit light when heated consists of two localizes levels: an isolated electron trap and a recombination center. This approach is commonly called One-Trap-One-Recombination center(OTOR)model[9]. The simple scheme of one trap/one-center model is shown in Fig. 2.2[11].

Figure 2.2 depicts a simple energy level scheme consisting of two localized levels: one act as trap (TR) and the other act as recombination center(R), filled of concentration from in trap(n), filled of concentration from in recombination center(m), recombination probability coefficient(A_{mn}), total concentration from in trap(N) and

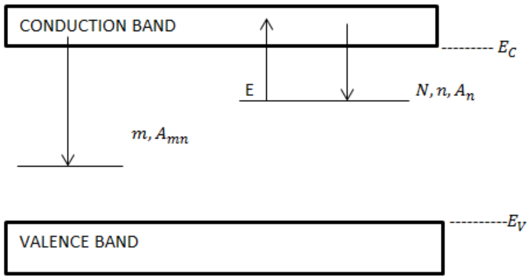

Figure 2.2: The allowed transitions (thermal excitation, retrapping and recombination) for the one-trap/one-centre model of TL.

retapping probability coefficient(A_n). It is also called *one trap and one recombination center* (OTOR) model. The traps are assumed to be electron traps and the recombination centers are hole traps. The traps and the recombination centers get filled up by the respective type of charge carriers following irradiation of the specimen. The electrons are ejected out of the traps (detrapped) and become free to move in the conduction band during the heating stage after absorption of enough energy, E.

During the random motion of the electrons in the conduction band following irradiation and thermal release, the electrons may recombine with holes trapped at recombination center (R) emitting light. Alternatively, the electrons may also fall back into an empty trap. This is called *retrapping.* Thus the transport of electrons from the traps to the recombination centers to emit luminescence may be described in terms of rate of excitation, retrapping and recombination. These three rates for the OTOR model are given by:

$$R_{ex} = ns \exp\left(\frac{-E}{kT}\right), \tag{2.6.1}$$

$$R_{ret} = n_c A(N - n), \tag{2.6.2}$$

and

$$R_{rec} = n_c A_r n_h, \tag{2.6.3}$$

where R_{ex}, R_{ret}, R_{rec}, respectively, are the excitation, retrapping and recombination rates, N and n, respectively, are the total and the filled concentration of the thermally active traps, n_c is the concentration of the charge carriers in the conduction band, n_h is the concentration of holes in the recombination center, 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, A and A_r, respectively, are the retrapping and the radiative recombination probability coefficients. The values of these coefficients depend on the capture cross-sections σ and σ_r of the traps and the recombination centers, respectively, expressed as:

$$A = \sigma v \qquad \text{and} \qquad A_r = \sigma_r v,$$

where v is the velocity electron in the conduction band.

The physical scheme used in formulating any particular model of TL determines the value of n_h. Since the overall charge neutrality condition should be ensured, the value of n_h is the sum of all the filled traps in the sample, which means that the filled active traps n and any deeper level traps which are thermally not affected, at the given temperature T. The fraction η of the excited carriers which produces luminescence during heating stage is given by the following equation

$$\eta = \frac{R_{rec}}{R_{ret} + R_{rec}} \tag{2.6.4}$$

Here, η is also called the luminescence efficiency and its value strongly depends on the values of the parameters in Eq. (2.6.1)-(2.6.3). However, the expression of η would change according to the applicable physical model since the denominator in Eq. (2.6.4) may increase depending on the existence of other possible routes of relaxation such as non-radiative recapture in deeper level traps.

2.6.2 Randall and Wilkins Model

Randall and Wilkins (RW) were the first to suggest a theoretical model for the TL emission [2]. They assumed that the retrapping may be negligible ($R_{ret} = 0$) and therefore according to Eq. (2.6.4), we have $\eta = 1$. This means that the TL emission intensity I is directly proportional to R_{ex} and hence given by

$$dn = -CR_{ex} = Cns \exp\left(\frac{-E}{kT}\right) dt, \tag{2.6.5}$$

where $T = T_0 + \beta t$ and 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. Rearranging Eq. (2.6.5), we have

$$\frac{dn}{n} = -s \exp\left(\frac{-E}{kT}\right) dt. \tag{2.6.6}$$

Assume that the sample is warmed up at a linear rate of heating, so that $dT/dt = \beta$ (Ks^{-1}). Equation (2.6.6) may then be written as:

$$n = n_0 \exp\left[-\frac{s}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) dT'\right]. \tag{2.6.7}$$

This model of TL comes under the category of first-order (FO) kinetics. The characteristics of the glow curves of this model are:

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

2. 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. The glow peaks for different E, for given values of s and b is shown in Fig. 2.4. It is seen that with increase in the

value of E the peak height is reduced, but the peak half width x, is increased, thus maintaining the area constant for a given value of n_0.

3. The temperature of maximum intensity, T_M increases almost linearly with E.

4. For given values of E and β, the glow peak shifts to lower T as s is increased (see Fig. 2.4). 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 x.

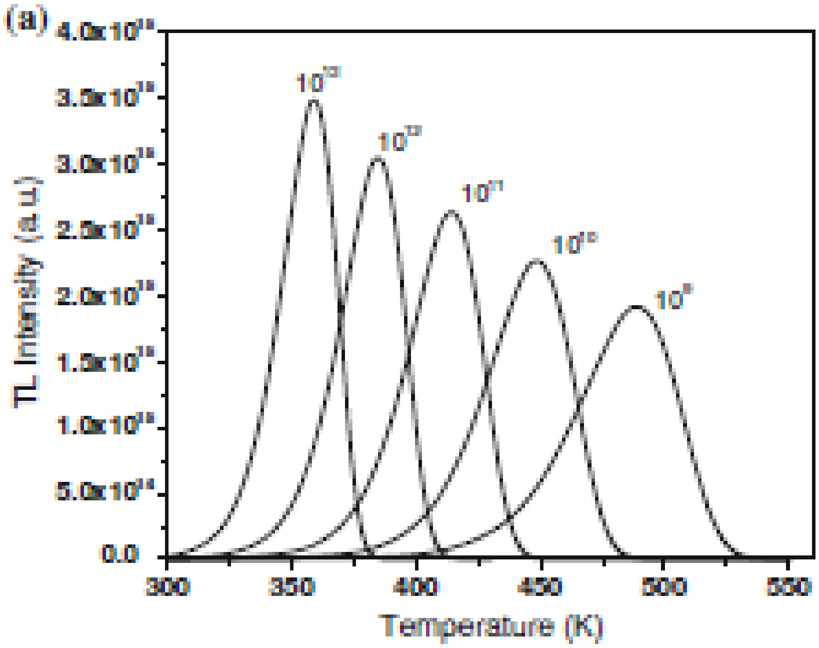

Figure 2.3: Change in temperature T_m of glow peak maximum with change in E. (a) Glow curves for $E = 0.5,\ 0.75,\ 1,\ 1.25$ and $1.5\ eV$, (b) T_m versus E. The values of s and b ...

2.7 Types of Order of kinetics

2.7.1 First-Order Kinetics

Randall and Wilkins, in 1945 assumed a mathematical expression for a peak in a glow curve. Their expressions were based on the energy band model and the well-known first-order kinetics. If the temperature and number of trapped electrons in the trap are kept constant. Thus, the decreases with time by the following expression [9]:

$$\frac{-dn}{dt} = -np, \tag{2.7.1}$$

where p is ....

Using Eq. (2.6.5) for n in Eq. (2.7.1) and integrating, one obtains

$$n = -n_0 exp\left[- s \int_{t_0}^{t} exp\left(- E/kT \right) dt \right] \tag{2.7.2}$$

where n_0 is the number of trapped electrons at the initial time $t_0 = 0$. Assuming now the following assumption[10]:

1. No electrons are released from the trap, when irradiation is switched off.
2. The Thermoluminescent material was T at low enough temperature.
3. In recombination centers, the luminescence efficiency is no dependent on temperature.
4. The recombination centers and concentrations of traps are no dependent on temperature.
5. In the conduction band, the life time of the electrons is short.
6. Negligible retrapping during the heat stage.

Therefore, according to the above mentioned assumptions, at a constant temperature, the intensity of luminescence emission becomes directly proportional to the rate of release of electrons from the trap. That is,

$$I = \frac{-dn}{dt} = Cpn, \tag{2.7.3}$$

where C is a constant of proportionality. Expression (2.7.3) is the equation of the decay phophorence at a constant temperature. For a linear increase in temperature at rate, $\beta = dT/dt$, Eq. (2.7.3) takes the form:

$$I_T = n_0 s \exp\left(\frac{-E}{kT}\right) \exp\left[\frac{-s}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E}{kT'}\right) dT'\right]. \tag{2.7.4}$$

2.7.2 Second-Order Kinetics

Garlick and Gibson, in 1948 they assumed in research of phosphorescence that two probabilities for a free charge carrier either recombination or being trapped within a recombination center. The term second order kinetic is utilized to explain a behavior in which retrapping is present.

$$I_T = \frac{-dn}{dt} = -s'n^2 \exp\left(\frac{E}{kT}\right), \tag{2.7.5}$$

where $s' = s/N$ is called *pre-exponential factor and constant* having dimensions of $cm^3 sec^{-1}$.

A second order kinetics based on such as Eq(2.6.12) are said to follow second order kinetics.The shape of the TL glow curve generated by Eq(2.6.12)is given by Garlik and Gibson[11]is

$$I(T) = -s'n^2 \exp\left(\frac{-E}{kT}\right) = \frac{n_0^2 s' \exp\left(\frac{-E}{kT}\right)}{\left[1 + \frac{s'n_0^2}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E}{kT'}\right) dT\right]^2} \tag{2.7.6}$$

2.7.3 GeneralOrder Kinetics

The first- or second-order kinetics do not explain the actual glow peak, so, in 1964, May and Partridge suggested a general-order expression to cover several cases.

$$I(T) = \frac{s''}{\beta} n_0 \exp\left(\frac{-E}{kT}\right)\left[1 + (b-1)\frac{s''}{\beta} * \int_{T_0}^{T} \exp\left(\frac{-E}{kT'}\right) dT'\right]^{-b/b-1}, \tag{2.7.7}$$

where s'' is $s'n_0^{b-1}$ with unit s^{-1}. In Eq. (2.7.7), it is help to deal with intermediate cases, and smoothly to first- and second-orders when $b \to 1$ and $b \to 2$, respectively.

2.8 Interactive Multiple Trap System

For the sake of simplicity, we consider interactive multiple trap system (IMTS) consists of the following: one active trap (AT), one recombination center (RC) and one thermally disconnected deep trap (TDDT); as shown in Fig(2.4). This means we are dealing with a glow curve with single peak. The various terms in the rate equations, i.e., excitation, retrapping, recombination, and recapture rates, for this scheme are:

$$R_{ex} = ns \exp\left(\frac{-E}{kT}\right), \tag{2.8.1}$$

$$R_{ret} = A_n(N-n)n_c, \tag{2.8.2}$$

$$R_{rec} = A_h(n+m+n_c)n_c, \tag{2.8.3}$$

and

$$R_{recap} = A_m(M-m)n_c, \tag{2.8.4}$$

where M and m are the total and the filled concentrations respectively of the TDDTs, and A_m is the capture coefficient of the TDDT and A_n and A_h are retrap coefficient probability and recombination probability coefficient respectively. The equations for the n, m, and n_c as a function of time, then, are

$$\frac{dn}{n} = -ns \exp\left(\frac{-E}{kT}\right) + A_n(N-n)n_c, \tag{2.8.5}$$

$$\frac{dn_c}{dt} = -ns\exp\left(\frac{-E}{kT}\right) - A_n(N-n)n_c - A_n(M-m)n_c - A_h(n+m+n_c)n_c. \quad (2.8.6)$$

Intensity of TL at any instant is given by the recombination rate at that instant:

$$I_{rec} = R_{rec} = A_h(n+m+n_c)n_c. \quad (2.8.7)$$

The concentration of RC is equal to $n+m+n_c$ so that it balances with the sum of the concentrations of the filled active traps n, filled TDDT m and the free electrons n_c in the conduction band.

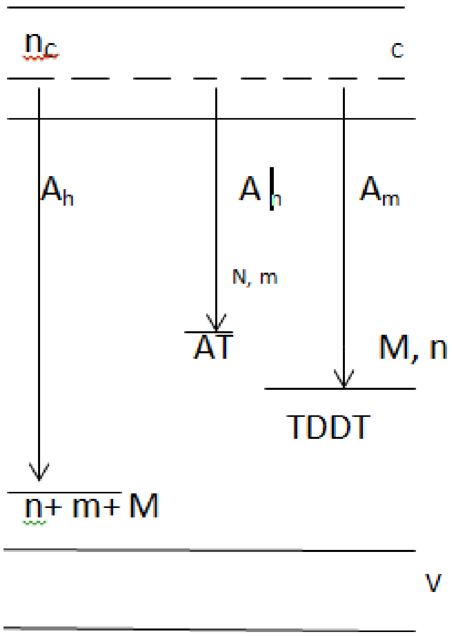

Figure 2.4: Simplified energy level scheme of the generalized model. It consists of one type of traps, one types RCs and one type of TDDs.

Remark: If we assume that the TDDTs do not recapture the free charge carriers during the TL read out heating, then the corresponding scheme is known as non-interactive multi-trap system (NMTS).

First-Order Kinetics

:

$$I(t) = -\frac{dn}{dt} = ns\exp(-E/kT). \tag{2.8.8}$$

By rearranging the above equation we get that:

$$\frac{dn}{n} = -s\exp\left[\frac{-E}{kT}dt\right]$$

and integrating this equation:

$$\int_{n_0}^{n}\frac{dn}{n} = -\int_{t_0}^{t} s\exp\left(\frac{-E}{kT'}\right)dt$$

and then we get

$$n = -n_0 exp\Big[-s\int_{t_0}^{t} exp\Big(-E/kT\Big)dt\Big]$$

From $T = T_0 + \beta t$ we get $dt = \frac{dT}{\beta}$ and substituting it in the above equation ,then

$$n = -n_0\int_{T_0}^{T}\left(\frac{s}{\beta}\right)\exp\left(\frac{-E}{kT'}\right)dT' \tag{2.8.9}$$

And substitute Eq(2.6.23) in Eq(2.6.22) we obtain

$$I(T) = n_0 s\exp(-E/kT)\exp\left[\frac{-s}{\beta}\int_{T_0}^{T} e^{-E/kT}\ dT\right], \tag{2.8.10}$$

And finally, It can be shown that the equations giving the maximum of glow peaks are evaluated by setting the derivative of Eqs. (2.8.10) respect temperature equal to zero. The results becomes

$$\frac{\beta E}{kT_M^2} = s\exp\Big(-\frac{E}{kT_M}\Big) \qquad (1^{st} - \text{order}), \tag{2.8.11}$$

Second-Order kinetics

:

$$I(t) = -\frac{dn}{dt} = \frac{-n^2}{N} s e^{-E/kT}, \tag{2.8.12}$$

When we re-arranging the above equation we get that

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

and integrating the above equation we get

$$n = \frac{n_0 N}{N + n_0 \left[\int_{t_0}^{t} s\left(\frac{-E}{kT}\right) dt\right]} \tag{2.8.13}$$

and substituting it in Eq (2.6.26)we get that

$$I(T) = n_0^2 \frac{s}{N} \exp(-E/kT) \left[1 + \frac{n_0 s}{N} \int_{t_0}^{t} \exp(-E/kT)\ dt\right]^{-2}, \tag{2.8.14}$$

From $T = T_0 + \beta t$ we get $dt = \frac{dT}{\beta}$ and substituting it in Eq(2.6.28) ,then we obtain

$$I(T) = n_0^2 \frac{s}{N} \exp(-E/kT) \left[1 + \frac{n_0 s}{\beta N} \int_{T_0}^{T} \exp(-E/kT^{'})\ dT^{'}\right]^{-2}, \tag{2.8.15}$$

And finally, It can be shown that the equations giving the maximum of glow peaks are evaluated by setting the derivative of Eqs. (2.6.29), equal to zero. The results becomes

$$\frac{\beta E}{kT_M^2} = s \exp\left(-\frac{E}{kT_M}\right)\left[1 + \left(\frac{2kT_M}{E}\right)\right] \qquad (2^{nd} - \text{order}), \tag{2.8.16}$$

General-Order Kinetics

:

$$I(t) = -\frac{dn}{dt} = -n^b s^{'} e^{-E/kT}. \tag{2.8.17}$$

and r-aaranging the above equation,becomes

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

and integrating this equation,

$$\int_{n_0}^{n} \frac{dn}{n^b} = \int_{t_0}^{t} s^{'} \exp\left(\frac{-E}{kT}\right) dt$$

Then

$$n = \frac{n^b}{n_0} \int_{t_0}^{t} s^{'} \exp\left(\frac{-E}{kT}\right) dt \tag{2.8.18}$$

From $T = T_0 + \beta t$ we can determine $\frac{dT}{\beta} = dt$ and substitute in Eq(2.6.32)the result become

$$n = \frac{n^b n_0}{n_0^b} \left[\int_{T_0}^{T} \left(\frac{s^{'}}{\beta}\right) \exp\left(\frac{-E}{kT^{'}}\right) dT^{'} \right] \tag{2.8.19}$$

and by substiting in Eq(2.6.31) we get that

$$I(T) = s^{'} n_0^b \exp\left(\frac{-E}{kT}\right) \left[\frac{(b-1)s^{'} n^{b-1}}{\beta} \int_{T_0}^{T} \exp\left(\frac{-E}{kT^{'}}\right) dT^{'} + 1 \right]^{\frac{b}{b-1}} \tag{2.8.20}$$

Where $s^{'} = s^{''} n_0^{b-1}$,then we obtain

$$I(T) = s^{''} n_0 \exp(-E/kT) \left[1 + \frac{s^{''}(b-1)}{\beta} \int_{T_0}^{T} \exp(-E/kT)\ dT \right]^{-\frac{b}{b-1}}, \tag{2.8.21}$$

and finally, the condition for maximum of TL intensity (T_M)in the glow curve is found by equation the derivative $(\frac{dI}{dt})$ of equation (2.6.35) to zero and it becomes

$$\frac{\beta E}{kT_M^2} = s \exp\Big(- \frac{E}{kT_M} \Big) \Big[1 + (b-1) \Big(\frac{2kT_M}{E} \Big) \Big] \quad (3^{rd} - \text{order}), \tag{2.8.22}$$

Chapter 3

Methods of Analysis of thermoluminescence

In this chapter we present about six different main methods used for the analysis of thermoluminescence. These are:

1. the initial rise methods,
2. analysis employing the whole TL Glow Curve,
3. peak position methods of analysis,
4. isothermal decay method,
5. methods of analysis based on the shape of the Glow Curve, and
6. curve fitting method.

3.1 Initial Rise Methods

The geometrical shape of TL glow peak plays an important role in calculating trapping parameters. in IR method, the initial rising porition of the peaK i.e, $T < T_M$(where T_M is the temperature at which the TL maximum occurs) is taken under consideration. In the law initial rise tall of a peak, the amount of trapped electrons can be assumed to be a constant, the dependence of temperature being negligible. The initial part of TL curve is exponential dependent on temperature according to $I(T) = constantx \exp(\frac{-E}{kT})$ (see figure 3.1)[13].

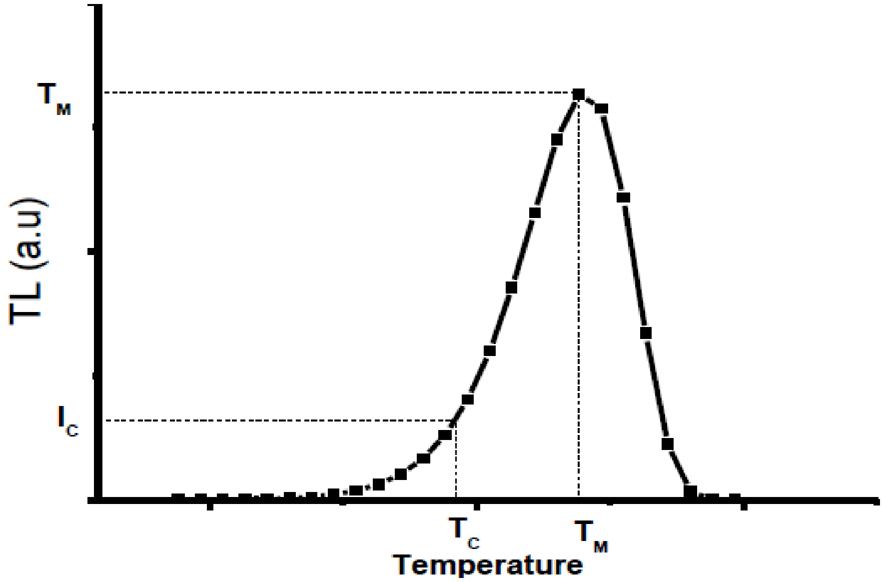

Figure 3.1: The initial rise part of a thermoluminescence glow curve.

Clearlly then, a plot of $\ln(I)$ versus $1/T$ over this initial rise region results in a straight line of slope $(\frac{-E}{kT})$ so the activation energy is easily found without any knowledge of the frequency factor [13].

3.2 Method Based on the Whole TL Glow Curve

The methods described in the initial rise method utilize only the initial rising portion of a glow peak, thus 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

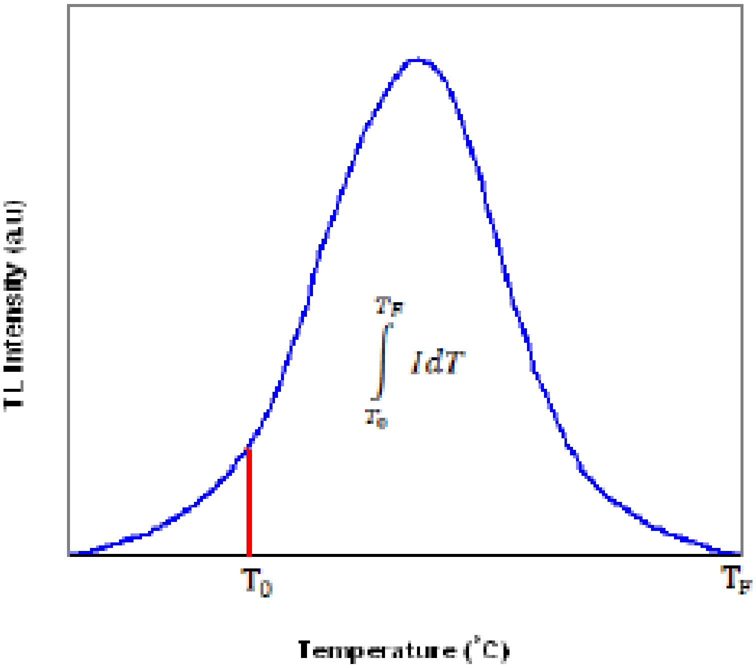

Figure 3.2: Calculation of the area n(T) in the whole glow peak measurement method.

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 T_L 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 Figure 3.2 [5].

$$n = \int Idt = \frac{1}{\beta}\int IdT \tag{3.2.1}$$

Assuming first order kinetics and substituting the Randall-Wilkins relation given in Eq. (2.6.22)

$$\frac{dn}{n} = -\frac{s}{\beta}\exp\left(\frac{-E}{KT}\right)$$

the following relation can be obtained

$$\ln(\frac{I}{\int IdT}) = \ln\left(\frac{s}{\beta}\right) - \frac{E}{kT} \tag{3.2.2}$$

From Eq. 3.2, one can see that in the case of first order kinetics, the term $ln[I/n(T)]$ is a linear function of E/kT with a slope -E and an intercept equal to $ln\left(s/\beta\right)$. May and Partride[15] and Montoni et al[14] proposed the same method in the case of general order kinetics. In this case the equation is

$$\ln(\frac{I}{n^b}) = \ln(\frac{s'}{\beta} - \frac{E}{kT'}) \tag{3.2.3}$$

which is graphically processed by plotting $\ln\left(I/n^b\right)$ versus $1/kT$. For the case when the order of kinetics b is known, one can obtain a broad range of temperatures in which the curve is a straight line. However, when the first order of kinetics is unknown, several lines are drawn with various values of b and the best straight line is chosen.

3.3 Peak Position Methods of Analysis

3.3.1 Methods of Analysis Based on Temperature at its Maximum Value

Randall and Wilkins in[7], they suggested that at the probability of charge release from a trap is unity

$$s\exp(-\frac{E}{kT}) = 1 \tag{3.3.1}$$

Or They were found expression for E, using a value $s = 2.9 * 10^9 s^{-1}$.

$$E = KT_m \ln(s). \tag{3.3.2}$$

Urbach in 1930, displayed the similar relation using $S = 2.9 * 10^9 s^{-1}$.

$$E = \frac{T_m}{500} = 23KT_m. \tag{3.3.3}$$

The equations mention above can be used only as a first approximation of the E values.

3.3.2 Methods Based on Various Heating Rates

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. Bohum, et al proposed a method of calculating E based on two different heating rates for a first-order peak. The maximum temperarure of the peak's change related to heating rate changes: at quicker heating rates correspond a shift temperature about higher rate. Bohum, et al suggested that the method to calculate based on two different heating rates for first-order peak.[17]

$$E = k\left(\frac{T_{M1}T_{M2}}{T_{M1} - T_{M2}}\right) \ln\left[\frac{\beta_1}{\beta_2}\left(\frac{T_{M2}}{T_{M1}}\right)^2\right]. \tag{3.3.4}$$

If T_M can be measured within accuracy of 1^0C, this method yields E within an accuracy of$5percent$ [17].

In 1958 Hoogenstraaten suggested the use of several heating rates to first-order equation for obtain the following linear relation:

$$\ln\left(\frac{T_M^2}{\beta}\right) = \frac{E}{kT_M} + \ln\left(\frac{E}{sk}\right). \tag{3.3.5}$$

Plotting $\ln(T_M^2/\beta)$ as a function of $1/(kT_M)$, one may obtain a straight line with slope E and an intercept $\ln[E/(sk)]$.

Chen and Winer, in 1970 reported a method which uses an approximation for the integral appearing in the general-order expression of $I(T)$, i.e., Eq. (2.8.21), obtained the following equation [17]:

$$\ln\left[I_M^{b-1}\left(\frac{T_M^2}{\beta}\right)^b\right] = \frac{E}{kT_M} + c, \tag{3.3.6}$$

where c is constant. Using Eq. (3.3.6), it is possible to evaluate the quantity on the left-side for different values of b, and to obtain a set of graphs as a function of $1/(kT_M)$. The value of b for which the graph best approximates linearity is found, and the graphs are fitted by a straight line whose slope is E. The method is valid for general heating rates, i.e., the heating rate β does not need to be constant. For the case of second-order kinetics ($b = 2$), Eq. (3.3.6) becomes

$$\ln\left[I_M\left(\frac{T_M^2}{\beta}\right)^2\right] = \frac{E}{kT_M} + c. \tag{3.3.7}$$

This method is useful only when b is appreciably different from unity, since for $b = 1$ the temperature T_M of maximum TL intensity is independent of the initial concentration n_0 of trapped electrons.

A different method that uses two heating rates was proposed in [15]. It is analogous to the Booth method, which is strictly valid for a first-order peak, but in this case it is applied to a non-first-order TL peak and it is based on the variation of I_M with the heating rate β, which is much faster than the variation of T_M with β. Using the general-order expression one obtains [17]

$$E = k\frac{T_{M1}T_{M2}}{T_{M1} - T_{M2}}\ln\left(\frac{I_{M1}}{I_{M2}}\right). \tag{3.3.8}$$

The maximum systematic error in the activation energy E when using Eq. (3.3.8) is less than 1% for any order of kinetics ($1.1 \leq b \leq 2.5$). [17]. It must be emphasized that during application of the variable heating rate methods of analysis, it is essential to have good thermal contact between the heating element in the TL apparatus and the sample.

3.4 Isothermal Decay Method

This method was first given by Randall and Wilkins (RW), in 1969. If we assume an isolated FO kinetics glow peak, its E value may be found by simply plotting its isothermal decay at different temperatures. The TL intensity $I(t)$ at various times t at any given temperature T is given by

$$I(t) = I_0 \exp\biggl(- P(T)t\biggr) \tag{3.4.1}$$

where I_0 is the intensity at $t = 0$ and $p(T)$ is the intensity decay rate constant at temperature T and is given by where

$$p(T) = s \exp\left(\frac{-E}{kT}\right) \tag{3.4.2}$$

One may plot ln $\left[I(t)/I_0\right]$ $versust$ at two temperatures, say T_1 and T_2 and obtain the corresponding $p(T_1)$ and $p(T_2)$ values from the respective slopes of the obtained straight lines. The ratio $p(T_1)/p(T_2)$ leads to the value of E as+[2]

$$E = \frac{kT_1T_2}{T_1 - T_2} ln\left[\frac{p(T_1)}{p(T_2)}\right] \tag{3.4.3}$$

The value of s may be found by substituting the value of measurement temperature T,the measured values of E and $p(T)$ in the above stated expression of $p(T)$. To improve the confidence in the obtained values of E and s, one may record the isothermal decay of the given sample at several temperatures, to obtain corresponding $p(T)$ values at the selected decay temperatures.

3.5 Methods Based on the Shape of the Glow Curve

This method is based on the shape of the peak use two or three points from the glow-curve. Generally, these are the maximum of the peak T_M, low-temperature TL and high temperature T_1 (as shown in Figure.3.3). However, the methods are depend on the order of kinetic.In the Figure the notations represent the following: $\tau = T_M - T_1$ 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 the $\mu = \frac{\delta}{\omega}$ is the so-called geometrical shape or symmetry factor. In (1953), Grossweiner was suggested first method to determine the trap depth kinetics.

$$E = 1.51k\frac{T_MT_1}{T_M - T_1} \tag{3.5.1}$$

This expression explained on the first-order kinetics. For the first- and second-order kinetics, Lushchik was proposed method to calculate the E[15]. For the firstorder kinetics,

$$E = \frac{KT_M^2}{\delta} \tag{3.5.2}$$

Chen was modified equation mention above, by multiplying the 0.978, Eq. (3.13) [7]. Halperin and Braner produced a new formula by using the T_1 and T_2 on the glow curve.

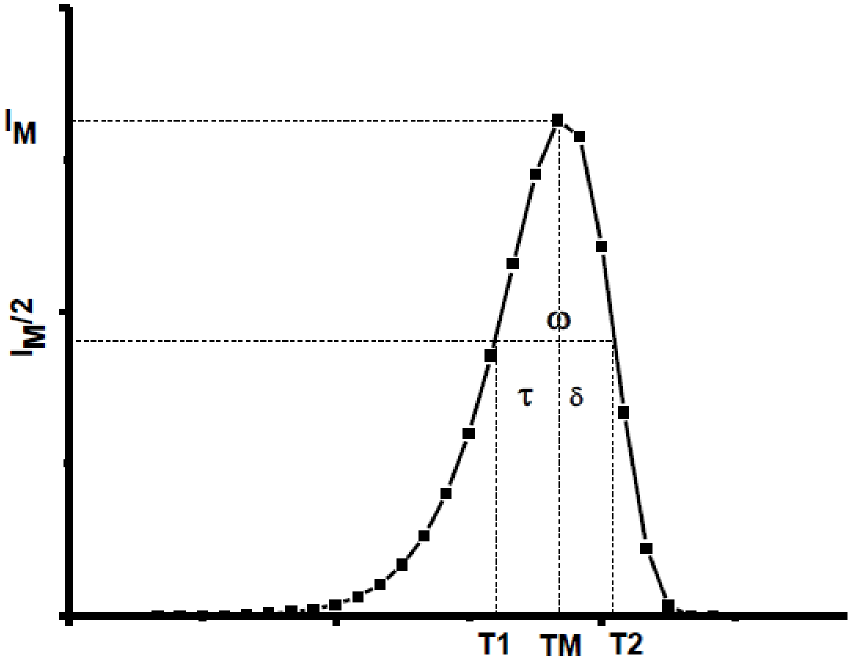

Figure 3.3: The geometrical shape of the glow

$$E = \frac{1.72}{\tau} KT_M^2 (1 - 2.58\triangle_M) \textit{for first order}, \tag{3.5.3}$$

with

$$\triangle_M = \frac{2KT_M}{E}. \tag{3.5.4}$$

Chen overcome the difficulty of the expression developed by Halperin and Braner which requires iterative process to find E. The new developed expression is given as

$$E = 2KT_M(1.25\frac{T_M}{\omega} - 1), \ \ \textit{for first order}, \tag{3.5.5}$$

Chen developed expressions to evaluate; this method does not use any iterative processes and no need any knows to the kinetic order [7].

$$E_\alpha = C_\alpha(\frac{KT_M^2}{\alpha}) - b_\alpha(2KT_M) \tag{3.5.6}$$

where α is, τ, δ or ω. The parameters of C_α and b_α are obtained as below:

$$C_\tau = 1.510 + 3.0(\mu - 0.42), b_\tau = 1.58 + 4.2(\mu - 0.42)$$

$$C_\delta = 0.976 + 7.3(\mu - 0.42), b_\delta = 0$$

$$C_\omega = 2.52 + 10.2(\mu - 0.42, b_\omega = 1$$

where $\mu = 0.42$ for the first-order kinetics.

3.6 Curve Fitting Methods

The method is to establish the approximate positions of the most prominent peaks in the glow- curve and to estimate initial values of E, S and β by using one of the analytical methods and its developed by Kitis et al[17]. For TL peaks following general order kinetics. The expression relies on two experimental measure quatities I_M(The maximum TL Intensity) and T_M (The temperature corresponding to the maximum TL intensity):

$$I(T) = I_M \exp[1+\frac{E}{KT}\frac{T-T_M}{T_M}-\frac{T^2}{T_M^2}(1-\frac{2KT_M}{E}*\exp(\frac{E}{KT}\frac{T-T_M}{T_M})-\frac{2KT_M}{E}] \tag{3.6.1}$$

Chapter 4

Results and Discussions

In this chapter, we seek to determine the concentration of electrons in the electron traps and the conduction band, the TL intensity as a function of temperature (the glow curve), The activation energy and the frequency factor for first-order kinetics by employing the method which is based on the various heating rates, β_i, where $i = 1,\ 2,\ 3,\ 4,\ 5,\ 6,\ 7$ and 8.

4.1 Glow Curves for Various Heating Rates

Figure 4.1 shows the graph of instantaneous concentration of electron in the conduction band as a function of temperature for a constant irradiation dose of $n_0/N = 0.5$ ($N = 10^{14}$ and eight different heating rates β_i, where $i = 1,\ 2,\ 3,\ 4,\ 5,\ 6,\ 7and\ 8$. It is observed that the concentration of electrons $n_c(T)$ decrease as the temperature increases just above 60^0C, reaching its minimum values approximately betweens 140^0C and 155^0C as the heating rates increase from $\beta_1 = 1.0Ks^{-1}$ to $\beta_8 = 4.5Ks^{-1}$, respectively. Moreover, it is seen from Fig. 4.1 that for temperatures approximately between

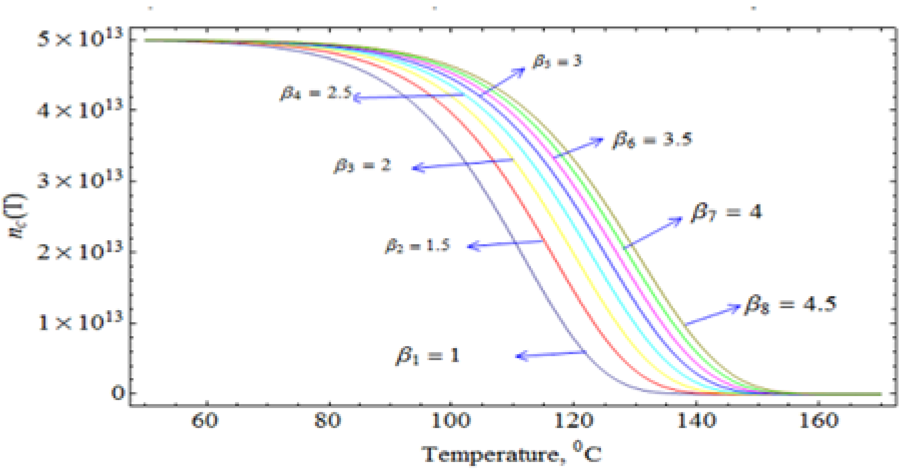

Figure 4.1: The concentration of electrons in the conduction band as a function of temperature for irradiation dose $n_0/N = 0.5$ and different heating rates, β. And $E_1 = 1, s_1 = 10^{12}, K = 8.617, N1 = 10^{14} and N Points = 170$

$60 - 155^0C$ the cures of n_c versus T show slight shifts with respect to each other towards high temperature values with an increase of the heating rate from$\beta_1 = 1.0Ks^{-1}$ to $\beta_8 = 4.5Ks^{-1}$.

Figure 4.2 shows the graph of the TL intensity as a function of temperature for the irradiation dose of $n_o/N = 0.5(N = 10^{14}cm^{-3})$ and eight different heating rates $\beta_i where i = 1,\ 2, .., \ 8$. It is observed that when the heating rate increases, the TL intensity decreases, while the peak temperatures shift to wards higher values with an increase of the heating rate. For instance, the maximum intensity is $I_{M_1} = 1.531x10^{12} counts/K$ for $\beta_1 = 1.0Ks^{-1}$ and $I_{M_8} = 1.531x10^{12} counts/K$ for $\beta_8 = 4.5Ks^{-1}$. Further, Fig. 4.2 shows that the width of the glow curves become broader and broader (e.g., the half widths are $w_{\beta_1} = T_2 - T_1 = (124.0 - 94.2)^0C) = 29.8^0C for \beta_1 = 1.0Ks^{-1}$ and $w_{\beta_8} = T_2 - T_1 = (144.1 - 111.3)^0C) = 32.8^0C$ for $\beta_8 = 4.5Ks^{-1}$: so that $\triangle w = 3^0C$). with an increase in the heating rate. It is well

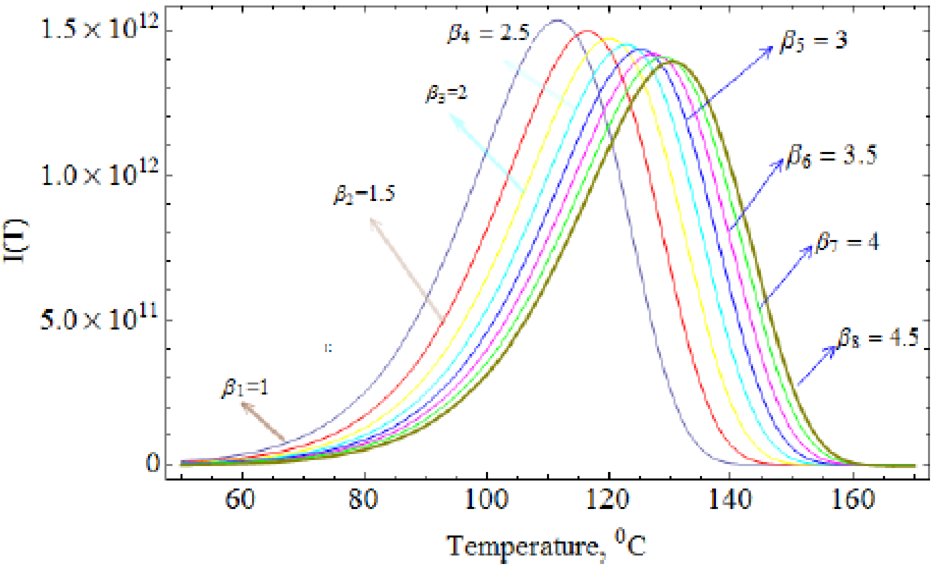

Figure 4.2: The TL intensity as a function of temperature for irradiation dose $n_0/N = 0.5$ and different heating rates, β. And $E_1 = 1, s_1 = 10^{12}, K = 8.617, N1 = 10^{14} and NPoints = 170$

.

known that the size of the width is associated with the dissipation (scattering) in a material medium[18]. Hence, it means that as the heating rate increases, the dissipation in the system is also increased which is reflected via an increased broadening of the width of the *glowcurve*.

The instantaneous concentration of electrons in the conduction band as a function of temperature are depicted in Fig. 4.3 for a constant irradiation dose of $n_0/N = 1.0$ ($N = 10^{14} cm^{-3}$) and eight different heating rates β_1, where $i = 1,\ 2, .., \ 8$. Similar to that observed in Fig. 4.1, it is found out that the instantaneous concentration of electrons in the conduction band (n_c) decreases as the temperature increases just above 60^0C, attaining minimum values between 135^0C and 155^0C as the heating

$\beta(K/s)$	$T_M(^0C)$	$T_M(K)$	$1/(kT_m)$	$\ln(T_m^2/\beta)$	$I_M(count/s)$	$I_M(count/K)$
1.0	111.7	384.7	30.166	11.905	1.531×10^{12}	1.531×10^{12}
1.5	116.6	389.6	29.787	11.525	1.499×10^{12}	09993×10^{12}
2	120.2	393.2	29.514	11.256	1.469×10^{12}	0.7345×10^{12}
2.5	123.9	396.9	29.239	11.051	1.466×10^{12}	0.5792×10^{12}
3	125.4	398.4	29.129	10.876	1.433×10^{12}	0.4776×10^{12}
3.5	127.7	401.7	28.991	10.732	1.422×10^{12}	4.062×10^{12}
4	128.7	403.3	28.890	10.603	1.41×10^{12}	0.3525×10^{12}
4.5	130.3	403.6	28.775	10.495	1.392×10^{12}	0.3093×10^{12}

Table 4.1: Computation of $\ln(T_M^2/\beta)$ and $1/(kT_M)$ for first order glow curve for irradiation dose $n_0/N = 0.5$.

rates from $\beta_1 = 1.0$ and $\beta_8 = 4.5Ks^{-1}$. Furthermore, it is seen that for temperatures between 60^0C and 155^0C the curve of n_c versus T show slight shifts towards high temperature values as the heating rate is increased from $1.0Ks^{-1}$ to $4.5Ks^{-1}$.

Figure 4.4 shows the graph of the TL intensity as a function of temperature for the irradiation dose of $n_0/N = 1.0Ks^{-1}(N = 10^{14}cm^{-3})$ and eight different heating rates β_i, where $i = 1,\ 2, .., \ 8$. Similar to that of found in Fig. 4.2, it is seen that when the heating rate increases, the TL intensity decreases and the peak temperatures shift to ward higher values. In particular, the peak intensities are $I_{M_1} = 3.068x10^{12}counts/K$ and $I_{M_8} = 2.797x10^{12}counts/K$ corresponding to the heating rates $\beta_1 = 1.0Ks^{-1}$ and $\beta_8 = 4.5Ks^{-1}$, the half-widths are $w_{\beta_1} = T_2 - T_1 = (124.0 - 94.2)^0C = 29.8^0C$ and $w_{\beta_8} = T_2 - T_1 = (144.1.0 - 111.4)^0C = 32.7^0C$; respectively, and hence the width changes by $\triangle w = 2.9^0C$.

At this point, it is worth noting the fact that independent of the value of the irradiation dose, n_o/N, the change in $\triangle w$ is constant within experimental error. This is not just a coincidence but is a valid fact for any first-order glow curve - w being a function of T_1 and T_2(indirectly also of T_M), our numerical analysis displayed in Table 4.1 and 4.2 clearly shows that the corresponding peak temperatures (T_M) for

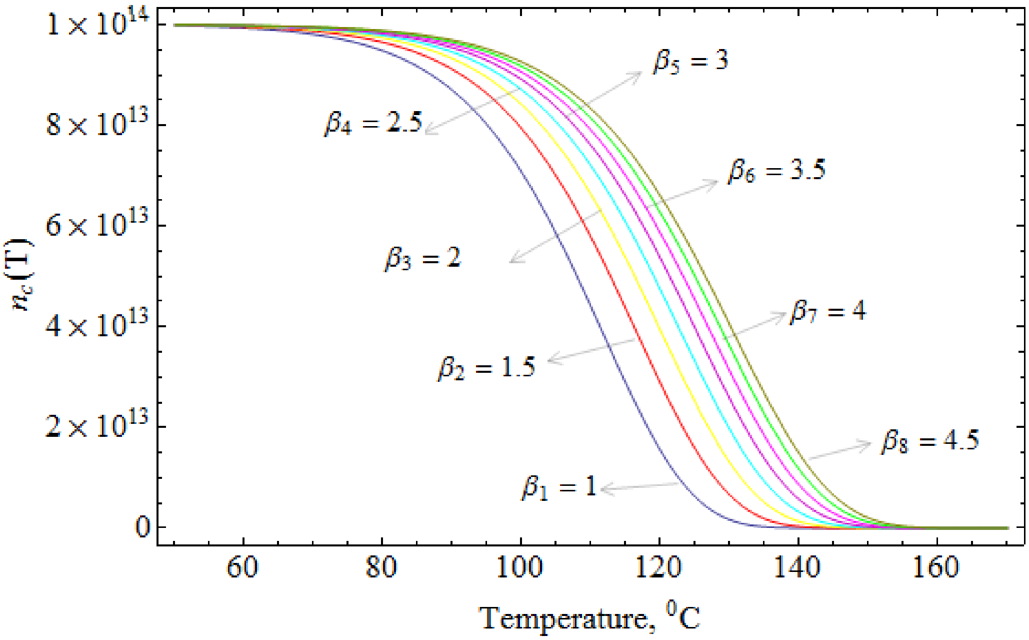

Figure 4.3: The concentration of electrons in the conduction band as a function of temperature for irradiation dose $n_0/N = 1.0$ and different heating rates, β. And $E_1 = 1, s_1 = 10^{12}, K = 8.617, N1 = 10^{14} and N Points = 170$

a given heating are almost the same both for $n_0/N = 0.5$ and $n_0/N = 1.0$. In short, our numerical analysis validates the fact that for first-order kinetics the maximum peak temperature(and the corresponding temperatures at half-widths T_1 and T_2) is independent of the irradiation dose- only the TL intensity changes as n_0/N changes. Note that for a given temperature and corresponding heating rates comparison of the intensities of the glow peaks depicted in Figs. 4.2 and 4.4 shows the intensities for $n_0/N = 1.0$ are larger than that for $n_0/N = 0.5$. This is due to the fact that with all other parameters kept constant, the TL intensity is directly proportional to the irradiation dose, n_0/N.

For further analysis, i.e., to determine the activation energy E and the frequency factor s, the relevant parameters corresponding to the glow peaks of Figs. 4.2 and

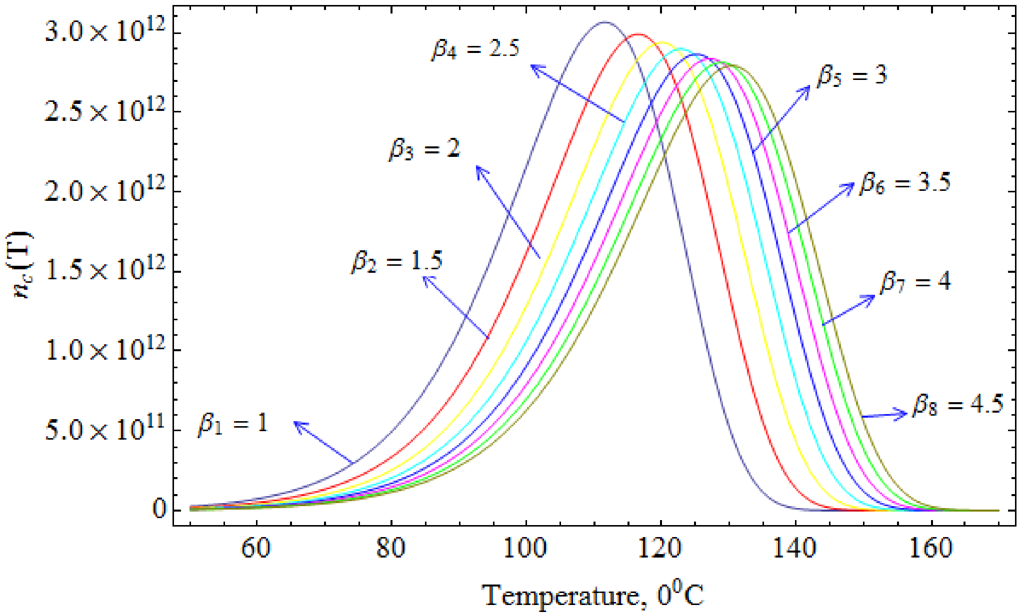

Figure 4.4: The TL intensity as a function of temperature for irradiation dose $n_0/N = 1.0$ and different heating rates, β. And $E_1 = 1, s_1 = 10^{12}, K = 8.617, N1 = 10^{14} and NPoints = 170$

.

4.4 are presented in Tables 4.1 and 4.2, respectively. At this point, it worth noting that sixth column of Tables 4.1 and 4.2 represents the peak temperatures of the TL glow curve in units of $counts/s$ is not suitable to analyze the actual TL glow curve which is a function of temperature. Therefore, it is necessary to convert the units into $counts/temperature$ (specifically in $counts/K$), which is done by dividing each values of column six of Tables 4.1 and 4.2 by the corresponding heating rates, $\beta_i = 1,\ 2, .., \ 8$. Note that for the graphs depicted in Figs 4.2 and 4.4, the intensities are expressed in $counts/s$ and hence the area under the curve is proportional to the heating rates; whereas for the corresponding graphs with the intensity expressed in $cuonts/temperature$, the area under glow curve is expected to be constant.

$\beta(K/s)$	$T_M(^0C)$	$T_M(K)$	$1/(kT_m)$	$\ln(T_m^2/\beta)$	$I_M(count/s)$	$I_M(count/K)$
1.0	111.5	384.5	30.182	11.904	3.068×10^{12}	3.068×10^{12}
1.5	116.5	389.5	29.795	11.524	2.993×10^{12}	1.995×10^{12}
2	120.1	393.1	29.522	11.253	2.935×10^{12}	1.4658×10^{12}
2.5	123.1	396.1	29.322	11.047	2.898×10^{12}	1.159×10^{12}
3	125.1	398.1	29.151	10.875	2.866×10^{12}	0.9553×10^{12}
3.5	127.2	400.2	28.998	10.732	2.866×10^{12}	0.8111×10^{12}
4	128.6	401.6	28.897	10.605	2.813×10^{12}	0.7032×10^{12}
4.5	130.2	403.2	28.782	10.495	2.797×10^{12}	0.6215×10^{12}

Table 4.2: Computation of $\ln(T_M^2/\beta)$ and $1/(kT_M)$ for first order glow curve for irradiation dose $n_0/N = 1.0$.

4.2 Activation Energy and Frequency Factor

During a thermoluminescence experiment, one typically obtains several glow curves under different conditions. For example, a series of TL glow curves may be obtained for a material that was irradiated at several doses. Usually the main goal of measuring and analyzing these TL glow curves is the extraction of several parameters that can be used to describe the TL process in the material. Among the important TL parameters are the activation energy (E) and the frequency factor. Below, employing the data extracted from Figs. 4.2 and 4.4, and displayed in Tables 4.1 and 4.2; the two parameters are computed used the methods based on various heating rates discussed in chapter 3.

4.2.1 Numerical Method to Determine E

(i) For the irradiation dose of $n_0/N = 0.5$, the activation energy (E) may be determine using Eqs. (3.3.4) and (3.3.8) That is, for the two heating rates (see Table 4.1) $\beta_1 = 1.0Ks^{-1}$ and $\beta_2 = 1.5Ks^{-1}$, we find that the peak temperatures are $T_{M_1} = 384.7K$ and $T_{M_2} = 389.6K$ and the corresponding peak intensities are $I_{M_1} = 1.531 \times$

$10^{12} counts/K$, $I_{M_2} = 0.9993 \times 10^{12} counts/K$, respectively. Hence, using Eq. (3.3.4), we obtain

$$E = \left[\frac{(8.617 \times 10^{-5})(384.7)(389.6)}{384.7 - 389.6}\right] ln\left[\frac{1}{1.5}\left(\frac{389.6}{384.7}\right)^2\right] = 1.002eV,$$

whereas using Eq. (3.3.8), we obtain

$$E = \left[\frac{(8.617 \times 10^{-5})(384.7)(389.6)}{384.7 - 389.6}\right] ln\left[\left(\frac{1.531 \times 10^{12}}{0.9993 \times 10^{12}}\right)\right] = 1.124eV.$$

(ii) For the irradiation dose of $n_0/N = 1.0$, for the heating rates (see Table 4.2, $\beta_1 = 1.0Ks^{-1}$ and $\beta_2 = 1.5Ks^{-1}$, we find that the peak temperatures are $T_{M_1} = 384.5K$ and $T_{M_2} = 389.5K$ and the corresponding peak intensities are $I_{M_1} = 3.068 \times 10^{12} counts/K$, $I_{M_2} = 1.995 \times 10^{12} counts/K$, respectively. Hence, using Eq. (3.3.4), we obtain

$$E = \left[\frac{(8.617 \times 10^{-5})(384.5)(389.5)}{384.5 - 389.5}\right] ln\left[\frac{1}{1.5}\left(\frac{389.5}{384.5}\right)^2\right] = 0.979eV,$$

and using Eq. (3.3.8), we get

$$E = \left[\frac{(8.617 \times 10^{-5})(384.5)(389.5)}{384.5 - 389.5}\right] ln\left[\left(\frac{3.068 \times 10^{12}}{1.995 \times 10^{12}}\right)\right] = 1.111eV.$$

Recall that the value of the activation energy used for the simulation is $E = 1.0eV$. In our case the values of E determined using the parameters generated from the glow curves are (a) $E = 1.002eV$ for $n_0/N = 0.5$ and $E = 0.979$ for $n_0/N = 1.0$, using Eq. (3.3.4); and (b)$E = 1.124eV$ for $n_0/N = 0.5$ and $E = 1.111eV$ for $n_0/N = 1.0$, using Eq. (3.3.8). It means that comparison of the results for E obtained using Eqs. (3.3.4) and (3.3.8), shows that the values obtained with the former are every closer to $E = 1.0eV$ (used for the simulation) than that obtained with the later. This may be explained with the fact that in the case of using Eq. (3.3.4) the only parameters required is T_M, whereas in Eq. (3.3.8) two parameters T_M and I_M needs to be 'measured' from the generated glow curve - and hence in the latter case the measurement error is compounded(error in T_M plus error in I_M) resulting to relatively large deviation.

4.2.2 Graphical Method to Determine E and s

In addition to the numerical method used in Section 4.2.1, the activation energy(E) as well as the frequency factor (s) can be3 determine by employing by the graphical method, i.e., from the graphs of $ln(T_M^2/\beta)$ versus $1/kT_M$. The corresponding graph is expected to be a straight line given by

$$ln\left(\frac{T_M^2}{\beta}\right) = \frac{E}{kT_M} + ln\left(\frac{E}{sk}\right).$$

with the slope being equal to E and the intercept with the vertical axis being equal to $ln[E/(sk)]$. Hence, using the graphically determined value of E (the slope), the frequency factor (s) may be determined from the graphically determined intercept $(ln[E/(sk)])$. That is,

$$s = \frac{E}{k} exp(-intercept) \tag{4.2.1}$$

For the glow curve shown in Figs. 4.2 and 4.4, the values T_M^2/β and $1/(kT_M)$ are calculated for different heating rates and displayed in tables 4.1 and 4.2. The corresponding graphs of $ln(T_M^2/\beta)$ as a function $1/(kT_M)$ are depicted in Figs. 4.5 and 4.6.

(i) For $n_0/N = 0.5$, we find that (see Fig. 4.5) the regression line given by the equation $y = 1.0081x - 18.492$ so that its slope is slope = 1.0081 and the intercept is intercept = - 18.492. Consequently, the activation energy corresponding to For $n_0/N = 0.5$ is equal to $E = 1.0081eV$. Then, using this value and the intercept, we find the frequency factor using Eq. (4.2.1). That is

$$s = \frac{0.9827}{8.617 \times 10^{-5}} exp(-18.492) = 1.256 \times 10^{12} s^{-1}$$

It is obvious that the graphically calculated value of s deviate from the value used for the simulation ($s = 10^{12}s^{-1}$). This may be due to personal error while reading

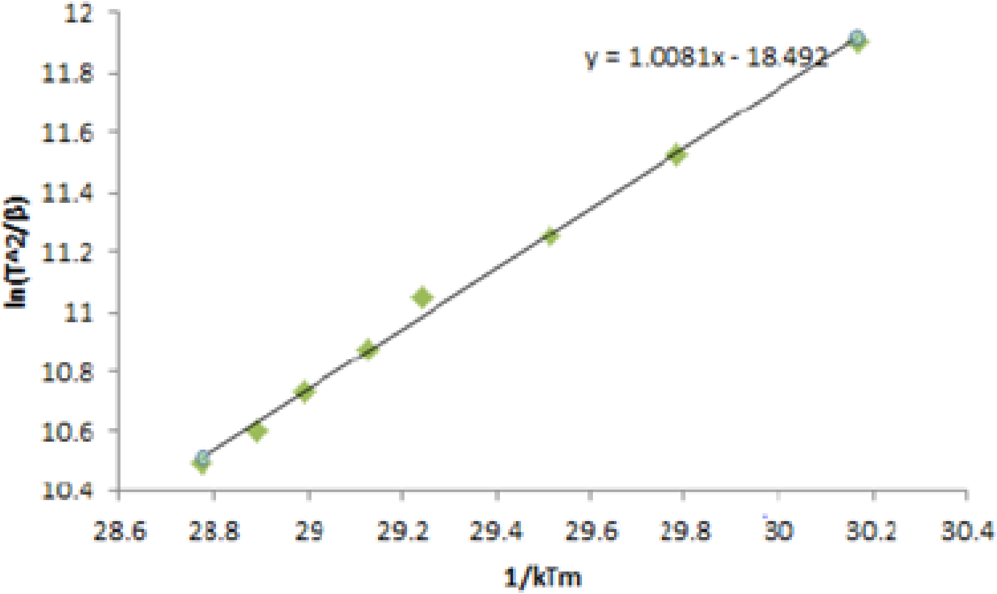

Figure 4.5: The graph of $ln(T_M^2/\beta)$ versus $1/(kT_M)$ for $n_0/N = 0.5$

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T_M from the stimulated value.

Alternatively, since the temperature T_M of the maximum TL intensity for a given heating rate is known from the numerically simulated data, the value of s can also be calculated by rearranging Eq. (2.6.25). That is, the frequency factor may be shown to be given by

$$s = \frac{\beta E}{kT_M^2} exp(E/kT_M) \tag{4.2.2}$$

For instance, from Table 4.1, we find that for $\beta_1 = 1.0Ks^{-1}$, $T_M = 384.7K$, Hence, employing the graphically determined value of the activation energy $E = 1.0081eV$, we obtain

$$s = \left[\frac{(1)(1.0081)}{(8.617 \times 10^{-5})(384.7)^2}\right] exp\left[\frac{1.0081}{(8.617 \times 10^{-5})(384.7)}\right] = 1.277 \times 10^{12}$$

(ii) For $n_0/N = 1.0$, we find that (see Fig. 4.6) the regression line is given by

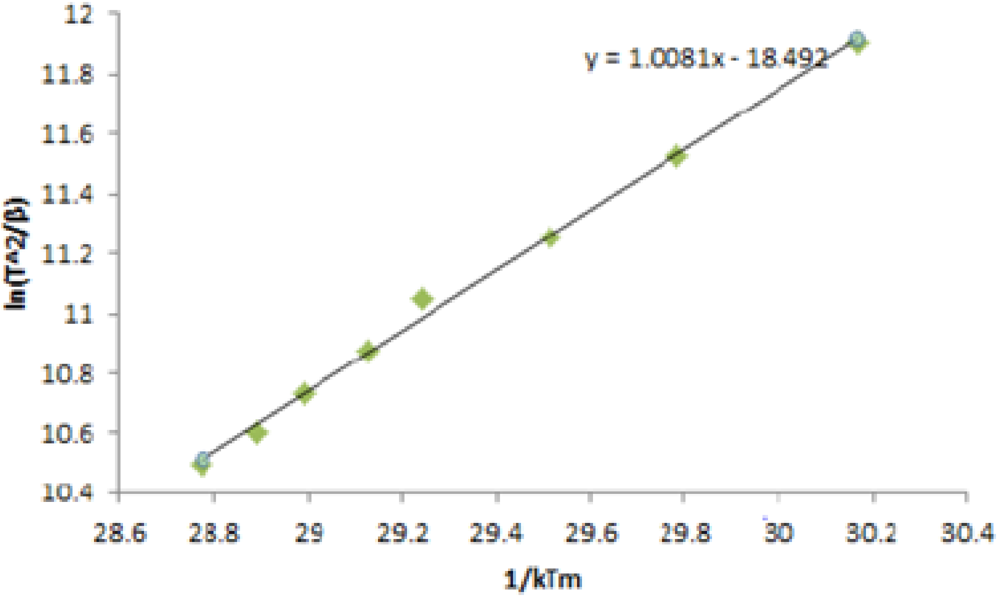

Figure 4.6: The graph of $ln(T_M^2/\beta)$ versus $1/(kT_M)$ for $n_0/N = 1.0$

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the equation y = 1.0078x = 18.504 so that the its slope is slope = 1.0078 and the intercept is intercept = - 18.504. Consequently, the activation energy corresponding to $n_0/N = 1.0$ is equal to $E = 1.0078$. Then, using this value and the intercept, we find the frequency factor to be

$$s = \left(\frac{1.0078}{8.617 \times 10^{-5}}\right) exp(18.507) = 1.255 \times 10^{12} s^{-1}$$

It is obvious that the graphically calculated value of s deviate from the value used for the simulation ($s = 10^{12} s^{-1}$ by $2.55 \times 10^{11} s^{-1}$. Similarly to the above case, the observed deviation my be due to personal error while reading T_M from the simulated value.

Also, from Table 4.2 for $\beta_1 = 1.0 K s^{-1}$, $T_M = 384.5K$, and employing graphically value of activation energy $E = 1.0078eV$, Eq. (2.6.25) results to

$$s = \left[\frac{(1)(1.078)}{(8.617 \times 10^{-5})(384.5)^2}\right] exp\left[\frac{1.078}{(8.617 \times 10^{-5})(384.5)}\right] = 1.283 \times 10^{12} s^{-1}.$$

In summary, for both irradiation does $n_0/N = 0.5$ and $n_0/N = 1.0$, Eq. (4.2.1) gives the value of the frequency factor which is closed to that used during the numerical simulation of the glow curve ($s = 10^{12} s^{-1}$ than that obtained using Eq. (4.2.2). Moreover, the activation energy obtained using graphical method is in an excellent agreement with that used for the simulation ($E = 1.0eV$) - a percentage error of less than 1*percent* and the frequency factor obtained using graphical method and used for the simulation $s = 10^{12} s^{-1}$ then the percentage error is 11*percent* this may be caused by personal error when he measure the temperature at the the peak of glow curve .

Chapter 5

Conclusions

In this work, we studied the TL phenomena by employing the one trap one recombination model and the method of various heating rates for irradiation dose of and $n_0/N = 1.0$. The TL intensity as a function of temperature and the instantaneous concentration of electrons in the electron traps and the conduction bands are simulated.

It is found that for a given irradiation dose the peak of the TL intensity decreases with an increases in the heating rate. Moreover, using parameters extracted from the simulated graphs of the glow curves, the activation energy and frequency factor are determined numerically and graphically. The calculated value of E and s are close to the value used to simulate the glow curves.

Furthermore, for the two irradiation dose used in the simulation, it is found that when the heating rate increases the peak of the glow curves shift to higher temperatures, the hight of the glow curve decrease and also the width of the glow curve increases. Finally, the slope of the graph for the irradiation dose $n_0/N = 1.0$ is obtained to be more closer that of the activation energy $E = 1.0$ than the irradiation dose $n_0/N = 0.5$, so can say that the graph becomes more straight for first-order kinetics when the irradiation dose of the traps is increase.

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DECLARATION

I, hereby, declare that this project is a review of previous works and that all sources of materials have been duly acknowledged.

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Place and time of submission:
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September 2018

This Project has been submitted for examination with my approval as University advisor.

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