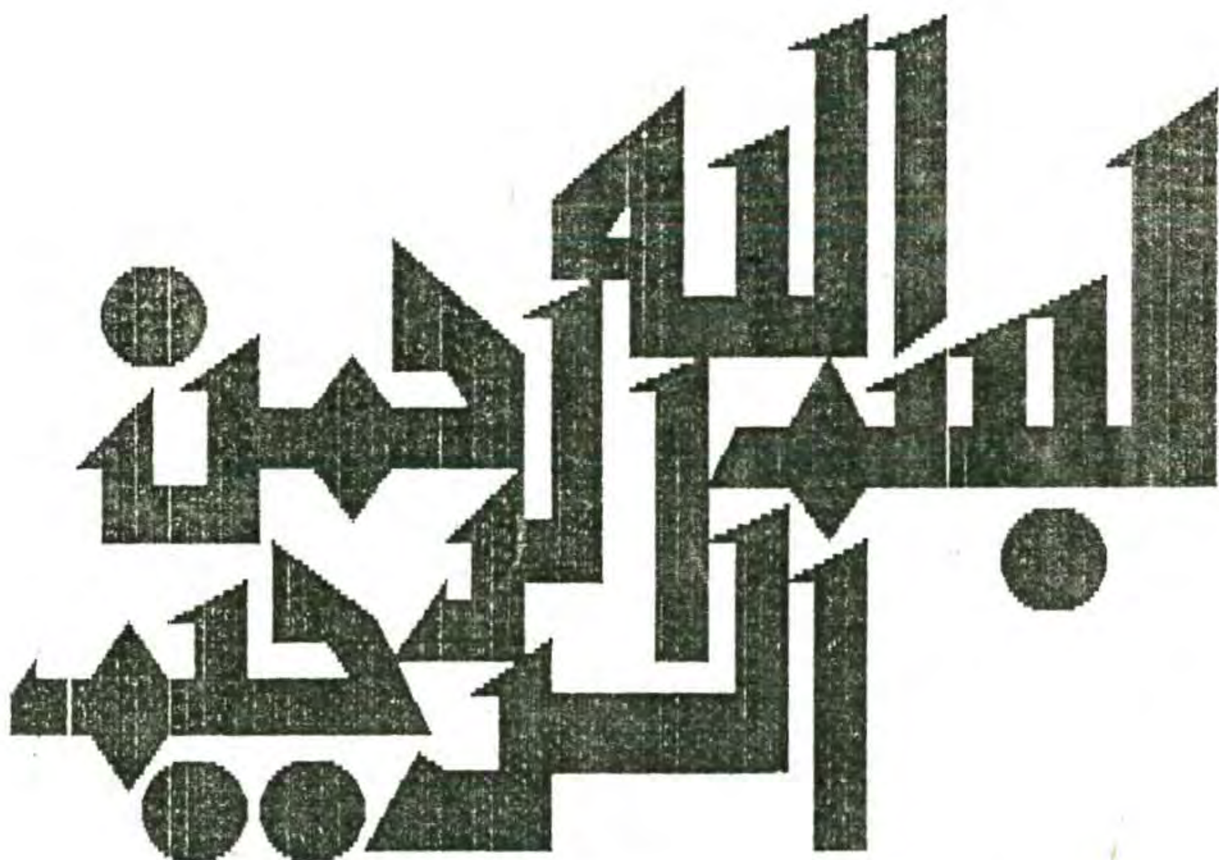

"In the name of ALLAH the Beneficient, the Merciful".

CHARACTERIZATION OF A MID–GAP DEEP ELECTRON LEVEL IN GaP.

BY

ASGHAR ALI

A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT

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1987

CERTIFICATE

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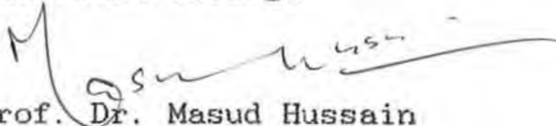

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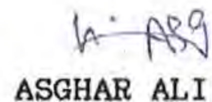

ASGHAR ALI

CONTENTS | Page

CHAPTER ONE	INTRODUCTION :	
1.1.	Historical Note.	1
1.2.	Crystal Defects.	3
1.3.	Electronic Defect State.	4
1.4.	Role Of Defect States.	5
1.5.	GaP As Light Emitting Diode.	6
1.6.	Significance Of Deep Level Work	6
1.7.	Motivation And Brief Description Of The Present Work.	7
CHAPTER TWO	PROPERTIES OF DEEP LEVEL :	
2.1.	Kinetic Processes — S.R.H theory.	10
2.2	Parameters Characterising Deep Levels.	15
2.3	Emission And Capture Mechanism.	17
2.3.1	Emission Rates	17
2.3.2	Capture Rates	20
2.3.3	Principle Of Detailed Balance	22
2.3.4	Trapping And Recombination	24
2.4	Effects Of Field On Deep Level Parameters	25
2.5	Effect Of Temperature On Deep Levels	31
CHAPTER THREE	TECHNIQUES	
3.1	P-N Junction Capacitance	36
3.2	Contribution Of Deep Levels To p-n Junction Capacitance.	38

3.3	Determination Of Deep Level Parameters From Dark Capacitance Transient Measurements	39
3.3.1	Thermal Emission Rates	39
3.3.2	Thermal Activation Energy	41
3.3.3	Deep Level Concentration	43
3.4	Dark Capacitance Transient Techniques	44
3.4.2	Thermally Stimulated Capacitance Transient Technique.	47
3.4.3	Deep Level Transient Spectroscopy	49
CHAPTER FOUR	**EXPERIMENTAL DETAILS:**	
4.1	Devices	54
4.2	C - V Measurements	54
4.3	Temperature Control System	56
4.4	Single Shot Measurements	56
4.5	Deep Level Spectroscopy Measurements	58
CHAPTER FIVE	**RESULTS AND DISCUSSION**	
5.1	C - V Measurements	60
5.2	Single Shot Measurements	60
5.3	DLTS Measurements	80
5.4	Combination Of DLTS And Single Shot Data	80
5.5	Concentration	90
5.6	Field Effect	93
5.7	Discussion	93

CHAPTER 1

INTRODUCTION

1.1. HISTORICAL NOTE :

In the known families of solids, the semiconductor constitute one of the most important classes. The advances in semiconductor theory and technology since second World War have provided stimulus to physicists, chemists and metallurgists in almost all fields of solid state research. In addition new electronic devices made from semiconductors have formed the basis of new industry and changed the nature of electronic engineering.

In the early part of the twentieth century Michael Faraday made one of the first experimental observations finding that silver sulphide had a negative temperature coefficient of resistance. The discovery of photo-voltage by Bacquerel in 1939 was another early observation. Nearly all the basic properties of the semiconductors were found in a very short span of time during the early years of the twentieth century, which reflects the extreme interest of the scientists in this area.

The most important effect in studying the mechanism of conduction in solids was discovered by Hall in 1879 which is known as Hall Effect. When the Hall Effect was applied to

semiconductors in 1930s, significant difference appeared between the conduction properties of semiconductors and metals. In particular the number of charge carriers were much less in semiconductors as compared with most metals, but charge carriers were generally somewhat more mobile in semiconductors. Moreover in semiconductors conduction took place by both positive and negative charge carriers.

The revolutionary effect that semiconductors have had on electronics since 1948 has resulted in some new branches of solid state physics. Existence of secondary ionization, tunnelling and surface effects predate the technological revolution of semiconductor devices, but the state of knowledge was extremely primitive.

The technology as well as associated theory of semiconductors advanced at a much accelerated pace as soon as single crystal semiconductors with controllable properties became available. In particular the first single crystal semiconductor that could be prepared with a high degree of perfection and purity was Germanium followed by Silicon. The techniques of preparation of single crystals of gallium arsenide , gallium phosphide and some other III-V compound semiconductors have been improved greatly in recent years. Good quality of crystals are now available with reasonable uniformity of properties such as doping density and mobility. A lot of work has been done to explore the properties of compound semiconductor and still there is a lot of work to be done and all this shows promise of finding technical applications.

It is a cherished dream of scientists to get pure crystals. A salient feature of the crystalline state is the regularity in the arrangement of atoms. The fact of regularity is an aid in obtaining conclusions about possible quantitative variety in the electrical behaviour of solids. In actual practice there are some imperfections in the crystalline state which are quite irremovable. These defects have a profound effect on the electronic properties of a semiconductor.

1.2 CRYSTAL DEFECTS:

The defects in a crystal can be divided in to three major classes:

i. Point defects.

ii. Line defects.

iii. Planar defects.

The defects which are atomic in size are known as point defects and are all local in nature. A point defect which may be a vacancy or an interstitial or substitutional impurity can bind a free electron or a hole in the potential well associated with it in a semiconductor. Schottky and Frenkel defects are two examples of such defects.

Line defects correspond to misplaced lines of atoms and boundaries of different orientations[1] in a crystal and are also named as dislocations. Edge- and screw-dislocations are the examples of line defects. Due to line defects the material around the dislocation has compressional or

dilational strains and results in both lowering and raising of the potential in the neighbourhood of the dislocations.

Planar defects correspond to misplaced planes of atoms and boundaries of different orientations in a crystal. Stacking fault and grain boundaries are the examples of planar defects.

1.3. Electronic defect states:

Defects caused by foreign atoms belonging to the closest groups in the periodic table to that of elemental semiconductors are localized . These localized states introduced by such atoms are donor or acceptor states[2]; these states lie close to the band-edge with binding energy of the ground state less than 50 meV. These levels are known as 'shallow' impurity levels, as these levels lie close to one of the energy band-edges, and are widely used in semiconductor device technology for modifying the nature and degree of electrical conductivity.

The result of native defects or of replacing an atom of the host lattice by an atom[3] which does not belong to an adjascent group of the periodic table are in the form of deep centres with binding energies much larger than those of shallow levels. Detailed studies of deep energy states have shown that both the measurements and their interpretation are usually far more difficult in compound materials than in elementary semiconductors due to residual impurities, non-stoichiometry and the formation of complexes.

1.4. ROLE OF DEFECT STATES :

GaAs and GaP crystals and devices after fabrication usually show trapping effects, caused by defect levels. The most important role of shallow donors and acceptors is to control conductivity. As their ionization energy is comparable to kT so these levels are completely ionized at room temperature and contribute to conductivity. These levels also contribute to resistivity as scattering centres, but this effect is secondary.

The fundamental role of deep levels in semiconductors is well established. An important consequence of the presence of deep impurities in semiconductors is the reduction in minority carrier life time. This can result in diodes with reverse recovery times in the nanosecond range. Deep impurities also play very significant role in limiting the light emitting efficiency of LEDs. A number of different experimental techniques have emerged over the years to characterise the deep levels each with its own specific advantages and emphasis. The near mid gap levels are known to be the focus of such studies because of their role as efficient recombination centres thus serving as 'killers' of carrier life time[4] and luminescence efficiency of common light-emitting diode (LED) materials like GaP.

Shockley, Read[5] and Hall[6] explained recombination as a successive capture of an electron and a hole by a deep state. According to them there are four processes through which recombination and generation takes place which are explained

in section.2.1.

1.5. GALLIUM PHOSPHIDE AS LIGHT EMITTING DIODE :

GaP is a semiconductor with an indirect band gap of 2.26 eV at 300 K . The indirect band gap can effectively be converted into direct band gap by introducing isoelectronic impurities . In other words these isoelectronic impurities introduce such energy levels within the forbidden gap which are localized in real space and are highly expanded in k-space and enhance the efficiency of the diode . The diodes having direct band gap are more efficient than diodes having indirect band gap because there is no phase difference between the conduction and valence band wave functions.

This difference in wave function in GaP can be ended by introducing isovalent impurities i.e. nitrogen replacing phosphorus atoms in the p-side of the GaP diode used for green emission , Zn-O[7] and Mg-O[8] complexes provide luminescent centres which emit light in the red and yellow wave lengths respectively

1.6 SIGNIFICANCE OF DEEP LEVEL WORK :

A good knowledge of impurity levels and their concentration is necessary to determine the general behaviour of a device. The techniques of preparation of single crystals of gallium arsenide, gallium phosphide and other III-V compound semiconductors have been improved greatly in recent

years. Good quality crystals are now available with reasonable uniformity of properties such as doping densities and mobility. In the course of these developments, doping has been studied for a wide spectrum of impurities. Most of these impurities produce energy levels deep in the energy gap. In some instances impurity pairing, or interaction with native defects occur that cause unexpected additions to the energy level structure. Semiemperical methods based on experimental results are the only means of getting knowledge about these things. Even though a large amount of research effort has gone on the physics of deep levels, they are still far from being well understood.

The understanding and formulation of basic deep level physics also requires more and more facts about deep levels to be brought into light . Therefore the interest in basic semiconductor physics itself motivates an enhanced activity in the experimental side .

1.7. MOTIVATION AND BRIEF DESCRIPTION FOR PRESENT WORK :

The green LEDs used in the present work were first probed in the course of an M.Phil research project carried out in this laboratory by Mushtaq Ahmad[9]. The work consisted of single shot measurementson the 0.85 eV hole level which emitts holes appreciably at and above room temperature[4] . Those measurements were taken from 302 K to 329 K. At highest temperatures the hole emission transient was followed by a very slow electron emission transient which indicate that a

deeper electron level exists in these diodes. This was of great interest since this would be an almost mid-gap level and hence extreemly important from the point of view of photoluminescence efficiency of these LED's. Subsequently another M.Phil thesis by A.Jabbar[10] in this laboratory was devoted to thermally stimulated capacitance (TSCAP) study of this deeper level. That study gave the activation energy of the mid-gap level to be 1.09 eV[4].

The TSCAP measurements provide the energy depth of a deep level but can not provide the emission rate data which serves as the signature of the deep level. This is done with single shot dark capacitance maeasurements and deep level transient spectroscopy(DLTS). The energy position obtained from these later techniques is also more accurate than that obtained by TSCAP.

The purpose of this work ,hence, was to perform single shot and DLTS measurements on this level to obtain emission rate data and activation energy to fully characterize this important level.

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CHAPTER NO. 2

PROPERTIES OF DEEP LEVELS

In this chapter the theory of deep levels is explained. In the first part the parameters which are required to explain the properties and to characterise a deep level are discussed. In the last sections the influences of field and temperature on parameters of deep levels are discussed.

2.1 KINETIC PROCESSES — S.R.H.THEORY:

There are two mechanisms through which an electron-hole pair recombination takes place. These are shown schematically is Fig.2.1. In the first type of recombination process the electrons from conduction band and holes from valence band recombine directly and we call this type of recombination as band to band recombination. There is no contribution of the deep levels in this type of recombination.

In the second type of recombination, the electrons from the conduction band are first captured at a level which lies some where in the band gap and then recombine with holes from the valence band.

It is well known[1] that in semiconductors the lifetime is extremely sensitive to the method employed in the preparation of the semiconductor samples which indicates that some defects are introduced during the fabrication process

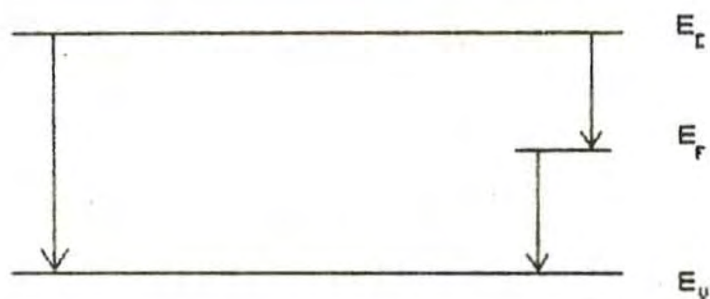

Fig. 2.1.

Illustration of the two mechanisms of Recombination

and their concentrations depend on the fabrication technique. These defects introduce energy levels within the forbidden gap and act as "stepping stones" in the transition of electrons and holes between the conduction and the valence bands. The recombination via such centres was worked out by Shockley and Read[2], and by Hall[3]. According to them if a deep level is present near the middle of the band gap having energy E_T then four basic emission and capture processes take place which are shown in Fig.2.2 In this figure E_C is the energy of the lowest state of the conduction band, E_V is the energy of the highest state of the valence band and E_T is the energy of deep centres. The arrows in the fig.2.2 designate the transition of electrons during a particular process.

Consider process (a) shown in Fig.2.2; the emission of electrons from the deep centres to the conduction band occurs at a rate proportional to the density of filled deep levels. If n_T is the density of filled deep traps then rate of emission r_a in this process is given as

$$r_a = e_n n_T \qquad 2.1$$

where e_n is the proportionality constant and is defined as the electron emission rate.

The capture of electrons by deep traps from the conduction band depends on the concentration of electrons in the conduction band and on the number of empty trap centres. If n is the number of electrons in conduction band and p_T is the concentration of empty deep states then the rate of process(b) in the fig.2.2. is given by

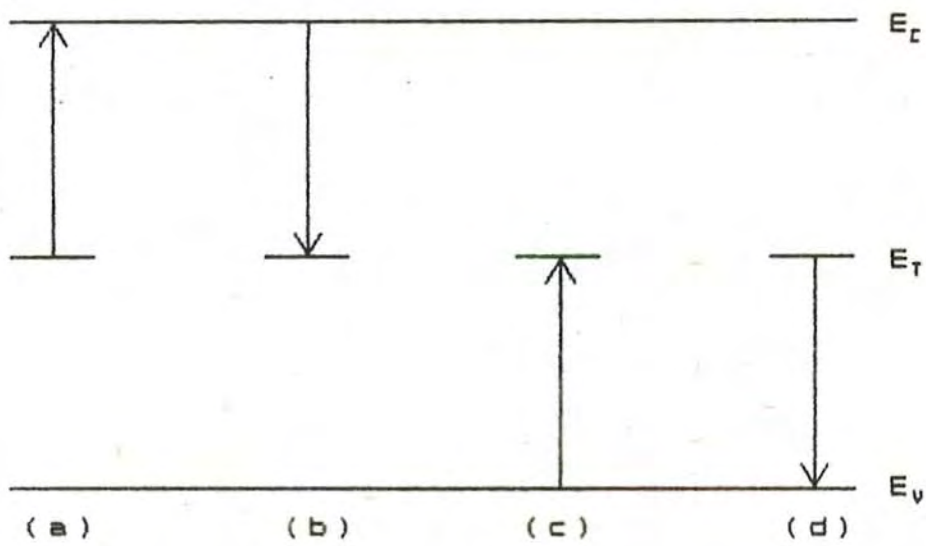

Fig. 2.2

Illustration of transitions taking place under non equilibrium conditions

$$r_b = C_n \, n \, p_T \qquad 2.2$$

where C_n is the proportionality constant and is defined as the capture rate of electrons.

The rate of process(c) i.e. emission of holes from the deep level to the valence band is proportional to the empty trap concentration. If empty trap concentration is p_T then rate of process (c) r_c is given as

$$r_c = e_p \, p_T \qquad 2.3$$

where proportionality constant e_p is defined as the hole emission rate.

Similarly the capture of holes by deep centres will depend on the density of holes in the valence band and also on the filled deep centres. If n_T is the filled trap density and p is the density of holes in the valence band then the rate of process(d) will be given by

$$r_d = C_p \, n_T \, p \qquad 2.4$$

where C_p is the proportionality constant and is defined as the hole capture rate.

By considering all the processes involving the conduction band, the net rate at which electrons leave the conduction band can be calculated. Thus:

$$-\frac{dn(t)}{dt} = r_b - r_a \qquad 2.5$$

$$-\frac{dn(t)}{dt} = C_n \, p_T \, n - e_n \, n_T \qquad 2.6$$

Similarly considering all the processes related to the valence band, the rate at which holes leave the valence band can be written as

$$-\frac{dP(t)}{dt} = r_d - r_c$$

$$= C_p\, n_T\, p - e_p\, p_T \qquad 2.7$$

By considering all the transitions at the deep centres, we can calculate the rate at which the density of filled trap increases.

$$\frac{dn_T(t)}{dt} = -\frac{dn(t)}{dt} + \frac{dp(t)}{dt}$$

$$= r_b - r_a - (\ r_d - r_c\ )$$

$$\frac{dn_T(t)}{dt} = C_n\, p_T\, n - e_n\, n_T - C_p\, n_T\, p + e_p\, p_T \qquad 2.8$$

If N_T denotes the total density of deep states then

$$N_T = n_T + p_T$$

$$p_T = N_T - n_T \qquad 2.9$$

By combining Eqs. 2.8 & 2.9 we get

$$\frac{dn_T(t)}{dt} = (\ n\ C_n + e_p)N_T - (e_n + n\ C_n + C_p P + e_p)n_T \qquad 2.10$$

The Eqs. 2.5, 2.6 and 2.10 are the kinetic equations which completely describe the electron or hole densities in the valence and conduction bands as well as in the deep levels at any time[4].

2.2. PARAMETERS CHARACTERIZING DEEP LEVELS:

The recombination processes of free charge carriers via deep centres has long been considered important in both applied and basic research. The free carrier life time

controls the properties of most semiconductor devices and recombination processes are frequently used to study important parameters of semiconductor materials. Recombination is often discussed in terms of radiation, cascade, multiphonon emission or Auger process. The particles involved are photons, phonons and charge carriers. In moderately doped semiconductors with indirect band gaps, the life time of free charge carriers is generally determined by recombination via energy levels in the forbidden energy gap. These energy levels may be due to shallow or deep centres originating from both intrinsic and extrinsic defects. The EL2 in GaAs and Gold in silicon are typical examples of life time controlling defects in semiconductors.

There are ten parameters which are usually used to characterize the deep levels. These parameters are E_T , $e^{o,T}_{n,p}$, $C^{o,T}_{n,p}$, and N_T. Where n stands for electrons related parameters , p for holes related parameters , T in subscript for deep traps. In superscript o stands for optical and T for thermal excitations.

The most important parameter characterizing deep level is its energy position inside the forbidden energy gap often denoted by E_T . The energy position for donor type traps is usually specified by $E_C - E_T$, which represents the ionization energy of trapped carriers from deep centres to the conduction band . The energy position for accepter type traps is represents by $E_T - E_V$ representing ionization energy from deep energy level into the valence band .

The emission rates of holes and electrons are

represented by e_p and e_n respectively . C_n and C_p represent the capture rates of electrons and holes respectively. The parameters which can be directly measured are capture rates and can be related to the capture cross-section denoted by σ_n and σ_p for electrons and holes respectively .

$$\sigma_{n,p} < V > = C_{n,p} \tag{2.11}$$

where < V > is the velocity of the carrier just before the capture[5]. N_T is the density of deep levels. The knowledge of density of deep sites is necessary,as the rates of generation and recombination of carriers depends on number of deep states.

2.3. EMISSION AND CAPTURE MECHANISM :

2.3.1. EMISSION RATE :

Emission of electron will take place from the deep centre to the conduction band and emission of holes will take place when an electron jumps towards deep centre from the valence band. Consider the Fig. 2.3. The process "a" represents the emission of electron from the centre to the conduction band . The emission rate of electron will be proportional to the concentration of the deep centres which are occupied by the electrons which is N_T F where F is the electron occupation probability. By using Fermi Dirac distribution function we can write

1

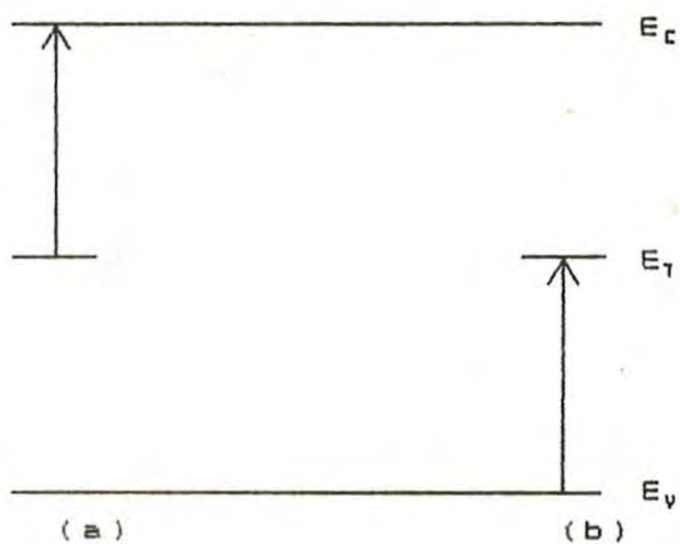

Fig. 2.3

Illustration of the Emission Rate

Processes

$$F = \frac{1}{1 - \exp\left(\frac{E_T - E_F}{k\,T}\right)} \qquad 2.11$$

So the emission rate of process "a" will be

$$r_a \propto N_T \, F \qquad 2.12$$

$$\Rightarrow \qquad r_a = e_n \, N_T \, F$$

where e_n is proportionality constant and is defined as the probability of an electron to jump into the conduction band from the occupied centre. By using detailed balance principle (explained in next section) one can find the emission rate of electron from the occupied centres to the conduction band as given below

$$e_n(T) = V_{th} \, \sigma_n \, n_i \, \exp\left(\frac{E_T - E_i}{k\,T}\right) \qquad 2.13$$

Similarly the rate of emission of holes from the empty centres to the valence band can be found. Obviously in Fig. 2.3 the rate of process "b" can be written as

$$r_b = e_p \, N_T \, (1 - F) \qquad 2.14$$

where the proportionality constant is e_p and is defined as the emission probability of the hole from the centre into the valence band . By using the detailed balance principle the net rate of emission of holes from the centre to the valence band is given by

$$e_p(T) = V_{th} \, \sigma_p \, n_i \, \exp\left(- \frac{E_T - E_i}{k\,T}\right) \qquad 2.15$$

where V_{th} is the thermal velocity of the carriers , n_i^2 is the total carrier concentration in the sample at equilibrium.

i.e. $n_i^2 = p \cdot n$.

2.3.2. CAPTURE RATES :

The capture mechanism of electrons and holes can be understood by considering Fig.2.4 where arrows indicate the opposite direction of the transition of a vacancy.

From process a in Fig.2.4 it is clear that capture of an electron from the conduction band to the centre or transition of a vacancy from the centre to the conduction band depends on the no. of vacancies of deep centres and no. of free electrons in the conduction band. As an electron can occupy only one centre, once a centre captures an electron, if can not capture any other electron. If N_T is the total no. of deep states then the no. of unoccupied states is given by

$$N_T\ (1 - F\ )$$

Then the rate of process "a" i.e. capture rate, is given by

$$r_a \propto n\ N_T\ (\ 1 - F\ )$$

$$r_a = \sigma_n\ V_{th}\ n\ N_T\ (\ 1 - F\ ) \qquad 2.16$$

where $V_{th}\ \sigma_n$ is a constant of proportionality, V_{th} is the thermal velocity of the carriers and σ_n is the capture cross-section which is the measure of how close the electron has to come to the centre to be captured.

In order to measure the capture rate of holes we consider the process "b" in Fig.2.4. According to this figure the electron emission by the centre to the valence band or the capture of hole by the centre from the valence band depends on the density of filled centres and the density of holes present in the valence band. In mathematical form

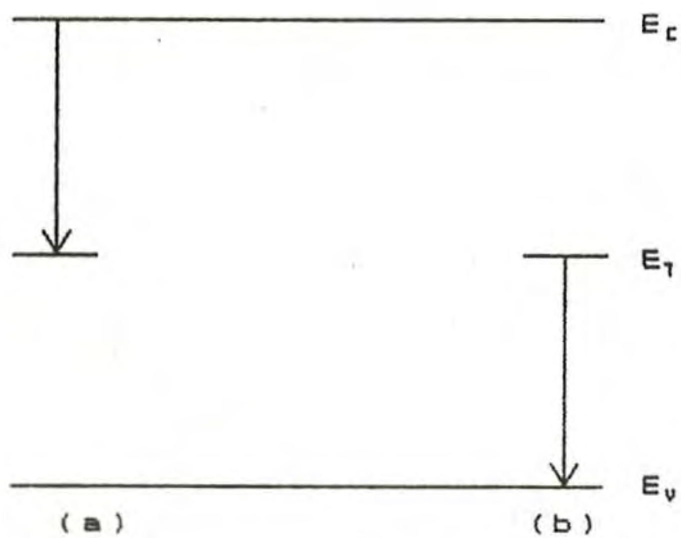

Fig. 2.4

Illustration of the Capture Rate

Processes

$$r_b = V_{th}\ \sigma_p\ p\ N_T\ F \qquad 2.18$$

where σ_p is the capture cross-section of holes and the product of thermal velocity and the capture cross-section is the constant of proportionality.

2.3.3. PRINCIPLE OF DETAILED BALANCE :

Detailed balance principle is used extensively in semiconductor statistics. Blackamore[6], Van Roosbroeck and shockley[7] derived the formulae concerning the carrier life time for intrinsic radiative recombination. Their approach was extended to the extrinsic radiative process by Sclar and Burstein[8] and Blackmore[6]. The rate of creation and annihilation of free carriers in a semiconductor must be carefully assessed in order to arrive at satisfactory characterization of the material. At thermal equilibrium each process and its reverse process takes place at equal rate. In this section we consider the sample at thermal equilibrium.

According to the detailed balance principle, the rate of emission of electron from the centre and the rate of capture of electron by the centre (Eqs. 2.1. and 2.2) are equal to each other. So we can write

$$C_n\ p_T\ n = n_T\ e_n \qquad 2.19$$

Similarly the rate of emission of holes by the centre and rate of capture of holes by the centre are equal. So according to detailed balance principle we can write

$$p\ n_T\ C_p = p_T\ e_p \qquad 2.20$$

Eliminating n_T and p_T from Eqs. 2.19 and 2.20. we get

$$e_n \; e_p = C_n \; C_p \; n \; p \tag{2.21}$$

Since by law of mass-action

$$n \; p = n_i^2 \tag{2.22}$$

$$\Rightarrow \qquad e_n \; e_p = C_n \; C_p \; n_i^2 \tag{2.23}$$

Which is the detailed balance relationship. The capture rate of electrons and holes at a deep centre is defined in Eq.2.11 i.e.

$$C_n = \langle V_n \rangle \sigma_n$$

$$C_p = \langle V_n \rangle \sigma_p$$

According to the detailed balance principle the rates of two processes which are involved in transition into and out of the conduction band, will be equal i.e. processes (a) and (b) in Fig.2.2.

$$r_a = r_b \tag{2.24}$$

Now the electron concentration is given by

$$n = N_c \; \exp\left[\frac{E_T - E_i}{k \; T} \right]$$

$$n = n_i \; \exp\left[\frac{E_T - E_i}{k \; T} \right] \tag{2.25}$$

So we can write

$$e_n = V_{th} \; \sigma_n \; n_i \; \exp\left[\frac{E_T - E_i}{k \; T} \right] \tag{2.26}$$

Similarly for holes, equating processes "c" and "d" shown in Fig.2.2 we get

As $$P = n_i \exp\left[\frac{E_i - E_T}{k\,T}\right] \qquad 2.27$$

$$\Rightarrow \quad e_p = V_p \; \sigma_{th} \; n_p \; \exp\left(\frac{E_i - E_T}{k\,T}\right) \qquad 2.28$$

Thus Eqs. 2.26 and 2.28 relate the emission rate to the capture cross-section and the energy depth of deep level.

2.3.4 TRAPPING AND RECOMBINATION :

A deep impurity in a semiconductor may act either as a trap centre or as a recombination centre. The behaviour of the deep impurity depends on the doping conditions, impurity temperature and cross-section. The occupancy of the centre in equilibrium and the way this occupancy is reached, can be determined from emission and capture rates. These values are functions of temperature, compensation and doping concentration.

A centre may be defined as trap centre, if a carrier captured by the centre stays there until it is re-emitted into the band where it comes from. It depends on the type of the captured carrier, whether it is a majority or minority trap centre. A centre acts as an electron trap when it collects an electron from the conduction band and after filling itself re-emits this electron to the conduction band. An empty centre may act as an electron trap when the probability of capturing an electron from the conduction band is much larger than emission of hole to the valence band or in notation form $C_e >> e_p$, and when centre is filled the probability of emission of electron to the conduction band is much larger than the capture of hole from the valence band or

in notation form $e_n >> C_p$ which is the case in Fig.2.5(a). Similarly Fig. 2.5(b) represents the case of a hole trap centre

If a centre acts as an generation centre i.e. when empty emits a hole to the valence band and when filled emits an electron to the conduction band, then this centre acts as a stepping stone for an electron in transition from valence band to conduction band i.e. generating an electron in conduction band and a hole in valence band. Such a centre is known as a generation centre and is represented in Fig 2.5(c).

Fig.2.5(d) represents a centre which when empty captures an electron from the conduction band and when filled captures a hole from valence band. So this centre acts as a stepping stone for an electron to recombine with a hole in the valence band. Hence such centres are known as recombination centres.

2.4. EFFECT OF FIELDS ON DEEP LEVEL PARAMETERS :

External perturbation such as electric field have long been used with some success in defect studies involving localized centres in insulators and semiconductors. The external perturbations introduce small characteristic splitting and also alter the level symmetry, which can be detected. The understanding of the level is more difficult as it requires more detailed knowledge of the electron charge distribution in the vicinity of the defect. The level separation introduced by external field is usually small and its value

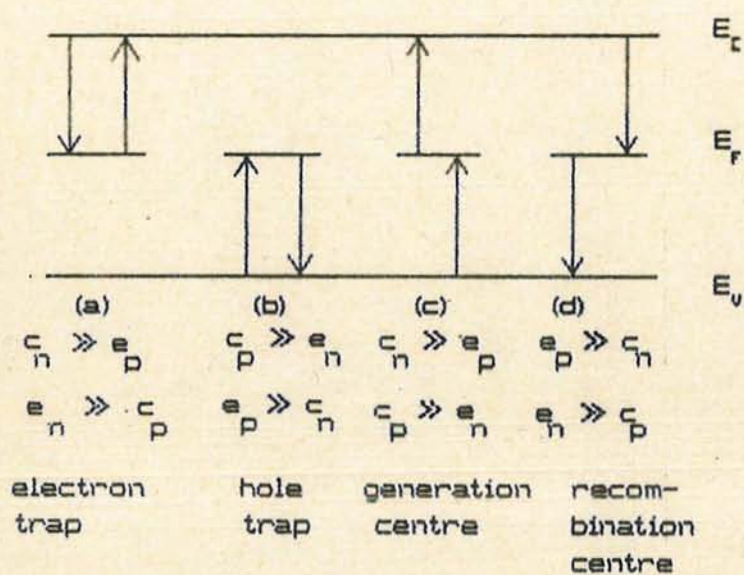

Fig. 2.5.

Definition and Illustration of the traps, Recombination and Generation centre

depends on many parameters.

Experimental methods based on thermal emission of electrons and holes are used to study the deep levels. According to Milnes[9] and Lang[10] the emission rate varies with

$$e_{(T)} = e_0 \exp\left(-\frac{E_T}{k_B\ T}\right) \qquad 2.29$$

where E_T the separation between the relevant band edge and the level. It is commonly assumed that the electric field affecting the defect is negligible. However the work of Tasch and Sah[11], Lang[10], Vincent et al[12] shows that there are some cases where emission rate does depend upon the applied bias voltage and doping.

The field dependence of the emission rate has normally been attributed to the Pool-Frankel barrier lowering $\Delta\phi$ (PF) indicated in Fig. 2.6.

The thermal emission rate for electrons in the presence of electric field is

$$e_n = e_{no} \exp\left(-\frac{E_T - \Delta E_T}{k_B\ T}\right) \qquad 2.30$$

In the Poole-Frenkel model, $\Delta E_T = e(eF/\varepsilon)^{1/2}$ is the correction factor, where e is the electron charge, F is electric field and ε is the static dielectric constant. It shows that correction factor ΔE_T depends only on the long range part of the impurity potential. The effect appears to be too weak to explain the field dependence for many deep levels. However the short range part of the impurity potential which is characteristic of deep centres may give rise to a tunnelling between the potential well and the conduction

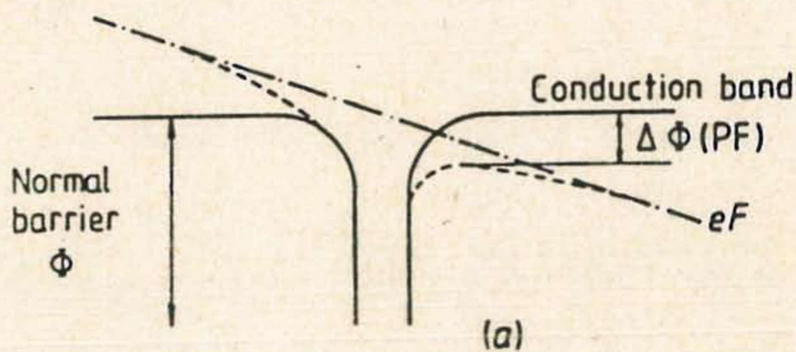

Fig. 2.6

Poole-Frenkel effect: the electric field F lowers the barrier ϕ normally associated with a defect possessing a long-range potential by $\Delta\phi(PF)$.

band as shown in Fig.2.7.

According to the work of Korol[13], the emission rate due to tunnelling is given by

$$e_n^T = \gamma \frac{E_T}{e_k} \exp(-k) \qquad 2.31$$

$$\text{where} \quad k = \frac{4}{3} \frac{(2m^*)^{\frac{1}{2}}}{e \hbar F} E_T^{\frac{3}{2}} \qquad 2.32$$

The exponential factor k is the classical expression for the transparency of the triangular barrier shown in Fig.2.7. The factor γ in Eq.2.31 depends on the form of short range potential and its value calculated by Korol is

$$\gamma = {}^{e}/_{3\hbar}$$

As the electric field varies linearly across the junction with distance d i.e.

$$F(x) \approx e N (d - X) \qquad 2.33$$

Where eN is the net charge density associated with shallow levels in the depletion region. X is the distance from the junction. This shows that the Eq.2.32 is field as well as bias dependent. So the change in the strength of $F(x)$ introduces some spatial distribution in emission rate[14].

2.5. EFFECT OF TEMPERATURE ON DEEP LEVELS :

The materials expand upon heating. With the variation of other material characteristics, band gaps also vary. For example, the fundamental band gap of GaAs changes by about 0.1 eV between 0 and 300 K. Almost the same figure is true

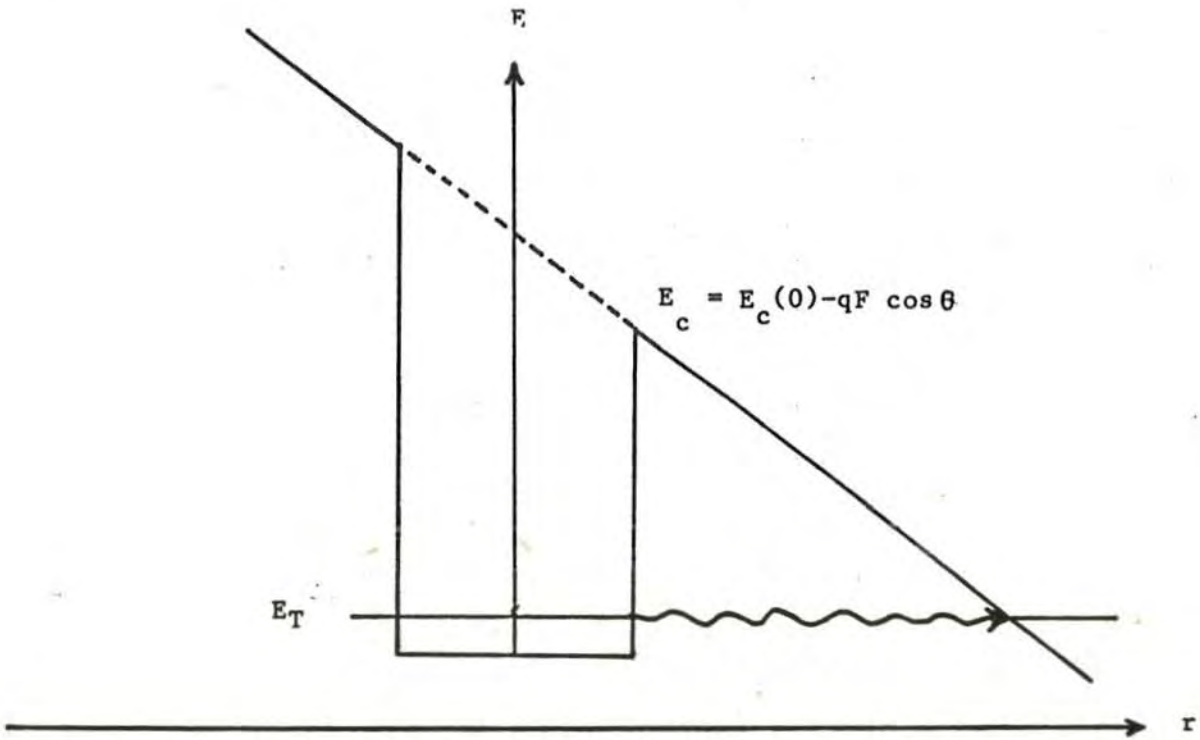

Fig.2.7

Schematic representation of electron tunneling from a Dirac well in an electric field.

for GaP. It is not easy to predict the changes in deep levels with temperature and must often be deduced from experimental data.

The band gap can be defined as the chemical potential ΔE_{cv} for electron hole pairs created by taking an electron from the top of the valence band into the conduction band. Thich is equal to the increase in Gibbs free energy G upon increasing the number of electron-hole pairs by one or to increase the internal energy U at constant entropy S and volume V for this increase in the electron-hole pair number. By using the first law of thermodynamics, ΔE_{cv} can be expressed in terms of enthalpy ΔH

$$\Delta E_{cv}(T) = \Delta H(T) - T\Delta S(T) \qquad 2.34$$

where $$\Delta S(T) = -\frac{\partial \Delta E_{cv}}{\partial T} \qquad 2.35$$

It was found by Thurmond[15] that ΔS is positive above T=0 and increase with increasing temperature so that according to Eq.2.33, ΔE_{cv} decreases with temperature. The experimental work done by Wong and Penchina[16]. They worked on silicon and obtained the data shown in Fig.2.8. The gap enthalpy can be obtained by linear extrapolation of $E_g(T)$ to T = 0 at any given point T as indicated by the broken line in Fig.2.8. The argument can be extended to the impurity problem by considering the gaps between the impurity level i and the relavent band (c,v), e.g. $\Delta E_{cv} \longrightarrow \Delta E_{ci}$. This ΔE_{ci} is the ΔE_T of the detailed ballence relationship.

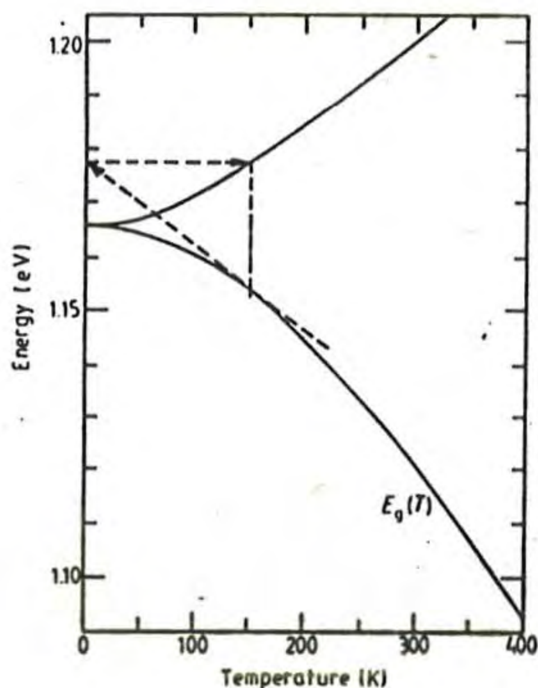

Fig.2.8.

The energy gap $E_g(T)$ of silicon as a function of temperature. The gap enthalpy (upper curve) can be obtained by linear extrapolation of $E_g(T)$ to T = 0 at any given point T as indicated by the broken line. (From Wong and Penchina 1975)[16].

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CHAPTER 3

TECHNIQUES FOR DEEP LEVEL CHARACTERIZATION

This chapter gives detailed information about the capacitance of a p-n junction diode and contribution of deep levels to the capacitance. Various dark capacitance transient techniques are thoroughly discussed in this chapter.

3.1 p-n JUNCTION CAPACITANCE:

Capacitance is defined as the differential flow of charge into a plate or terminal with respect to the change in voltage. When the voltage across a p-n junction changes, the depletion region width also changes. The number of minority carriers changes on both sides and result in resistive current flow as well as capacitive flow. The contribution due to change in depletion region to the capacitance is known as layer capacitance or junction capacitance, whereas the contribution due to the changes in minority carrier density is called diffusion capacitance.

Junction capacitance is dominant under reverse bias conditions and the diffusion capacitance is dominant when the junction is forward biased. In many applications of junction devices, the capacitance is a limiting factor in the usefulness of the device. On the other hand there are important applications in which the capacitance can be useful in circuit applications and in providing important information

about the structure of a p-n junction.

Consider a p-n junction with arbitrary distribution of impurities and contact potential V_B . If a reverse bias is applied to the diode, the total magnitude of the potential will be the sum of contact potential and the applied potential. The capacitance of such a junction can be defined as,

$$C = \frac{dQ}{dV} \quad 3.1$$

where dQ is the increase in the charge caused by a change in voltage for time dt resulting in a current ;

$$i = C \frac{dV}{dt} \quad 3.2$$

In a step junction diode, there is an abrupt change of ion concentration at either side of the junction interface and the junction potential V_J is given by

$$V_J = \frac{q N_D}{2 \varepsilon} \quad 3.3$$

where W is the depletion region width. The ε is ε_o ε_r, where ε_o is the permativety of free space and ε_r is the relative permativety of the material. The junction potential is also given by,

$$V_J = V_R + V_B \quad 3.4$$

where V_R is the applied reverse bias. The capacitance is given by

$$C = \frac{\varepsilon A}{W} \quad 3.5$$

In the case of an abrupt junction the transition region extends primarily into the least heavily doped side and the capacitance is determined by only one of the doping

densities. For a p^+n junction the capacitance is given by[1]

$$C = \frac{A}{2}\left[\frac{2 q \varepsilon}{V_J} N_D\right]^{1/2} \qquad 3.6$$

From the relation 3.6 it is also possible to obtain the doping densities of the lightly doped region from a measurement of junction capacitance.

If we take a linearly graded junction diode in which density of ions vary gradually, then the space charge density qN_D for such a junction varies as

$$V_J = \frac{q N_D}{12 \varepsilon} W^3 \qquad 3.7$$

Capacitance for a linearly graded junction is given by

$$C = A\left\{\frac{\varepsilon^2 q}{12 V_J} a\right\}^{1/3} \qquad 3.8$$

where a is the concentration gradient[2].

3.2 CONTRIBUTION OF DEEP LEVELS TO P-N JUNCTION CAPACITANCE

Suppose E_T is the energy position of a deep level and let the deep level has spatially uniform density N_T and the junction is placed under a reverse bias. For a steady state condition, the net rate of the charge leaving and coming towards the trap centre is zero i.e.

$$e_p N_T = (e_n + e_p) n_T \qquad 3.9$$

$$\text{or} \qquad n_T = \frac{e_p}{e_n + e_p} N_T \qquad 3.10$$

where equation 3.10 gives the density of filled traps under steady state condition. When the system is perturbed and then allowed to relax back, the number of filled traps changes and this will increase or decrease the total charge in the depletion region and hence the capacitance, which is given by equation 3.6 and 3.8 for step and linearly graded junctions respectively, will change. This change in capacitance is purely due to deep levels.

3.3 DETERMINATION OF DEEP LEVEL PARAMETERS FROM DARK CAPACITANCE TRANSIENT MEASUREMENTS :

If we chose a temperature somewhere in the range where the thermal emission rates of the carriers are appreciable to allow convenient measurements, the capacitance and current transients can be observed by placing the junction under perfect dark conditions.[3-7] The emission of carriers is obtained by thermal excitations after externally perturbing the system by applying reverse bias. The details about technique will be discussed in next section. In this section we discuss the basic principle of measuring the parameters of deep levels.

3.3.1. Thermal Emission Rate :

Consider a p^+n type of junction and also consider that an electron trap is present on n-side of the junction. The electron capture and electron emission processes will be

dominant. The net rate of electron emission is given by

$$\frac{dn_T}{dt} = C_n \, p_T \, n - e_n \, n_T \qquad 3.11$$

In steady state conditions the net change will be zero i.e. emission and capture processes are equal. If at time t = 0 an external perturbation i.e. reverse bias is applied then it will change the situation. The number of filled and unfilled trap centres will change due to this perturbation. The transient associated with return to steady state, is characterised at time $t = \infty$, i.e.

$$e_n \, n_T(\infty) = n \, C_n \, p_T(\infty) \qquad 3.12$$

The analysis of eq.3.12 provides useful information about the deep traps. In steady state conditions, a term can be defined as the change in filled and unfilled traps is equal i.e. $n_T = - p_T$ so the net rate of change of trapped electrons can be written as

$$\frac{dn_T}{dt} = C_n n \, p_T - e_n \, n_T$$

$$= (C_n n + e_n) \, \Delta p_T$$

OR $$\frac{dn_T}{dt} = - (C_n n + e_n) \, \Delta n_T \qquad 3.13$$

To solve the equation 3.13 we assume that $e_n + n \, C_n$ remains constant at a given position in time t. Then the solution of equation 3.13 can be written as

$$n_T(t) = n_T(0) \exp [-t(e_n n \, C_n)] \qquad 3.14$$

The value of C_n from equation 3.12 can be written as

$$C_n = \frac{e_n \, n_T(\infty)}{n \, p_T(\infty)}$$

putting this value in equation 3.14 we get

$$\Delta n_T = n_T(0) \exp \left[-te_n \left(\frac{p_T(\infty) + n_T(\infty)}{p_T(\infty)} \right) \right] \qquad 3.15$$

Now the occupancy factor may be defined as

$$F = \frac{n_T}{n_T + p_T} \quad \text{OR} \quad \frac{1}{1 - F} = \frac{n_T + p_T}{p_T} \qquad 3.16$$

Combining equations 3.15 and 3.16 we get.

$$F(t) - F(\infty) = (F_o - F_{(\infty)}) \exp \left(- \frac{t \, e_n}{1 - F_{(\infty)}} \right) \qquad 3.17$$

If final state is empty in that case $F_{(\infty)} = 0$ and Eq (3.17) can be written as

$$F(t) = F(o) \exp (- e_n t) \qquad 3.18$$

By taking log on both sides we get,

$$\ln \frac{F(t)}{F(o)} = - e_n t$$

$$\Rightarrow \qquad e_n = - \frac{1}{t} \ln \frac{F(t)}{F(o)} \qquad 3.19$$

Which is the inverse of time constant. Hence in principle emission rate can be calculated by measuring the time constant τ of the transient change in Δn_T.

3.3.2. THERMAL ACTIVATION ENERGIES :

According to the detailed balance principle the emission rate of carriers can be related to the capture cross-section as given below,

$$e_n = \sigma_n \langle V_n \rangle N_c \exp \left(- \frac{E_c - E_T}{k T} \right) \qquad 3.20$$

This equation gives the electron emission rate for electron trap and for hole trap emission rate can be written as

$$e_p = \sigma_p \langle V_p \rangle N_v \exp\left[-\frac{E_T - E_v}{k\,T}\right] \qquad 3.21$$

We consider here only the case of electron trap. If we consider temperature dependence of parameters, then we find that $V_{n,p}$ has $T^{1/2}$ dependence as $V^2 = \left(\frac{3\,k\,T}{m}\right)$

similarly $$N_{c,v} = 2\left[\frac{2\,\pi\,m^*_{e,h}\,k\,T}{h^2}\right]^{3/2}$$

Which shows that $N_{c,v}$ has $T^{3/2}$ dependence and $V_{n,p}$ has $T^{1/2}$ dependence. If the capture cross-section $\sigma_{n,p}$ has negligible temperature dependence but in some cases it does show temperature dependence then case eq.3.20, in terms of temperature can be written as

$$e_n \propto T^{1/2}.T^{3/2}.\exp\left[\frac{E_c - E_T}{k\,T}\right]$$

$$\Rightarrow \qquad \frac{e_n}{T^2} \propto \exp\left[\frac{E_c - E_T}{k\,T}\right] \qquad 3.22$$

taking log on both sides we get

$$\ln\frac{e_n}{T^2} \propto -\frac{E_c - E_T}{k\,T}$$

$$\Rightarrow \qquad \ln\frac{e_n}{T^2} \propto -\left[\frac{E_c - E_T}{k}\right]\frac{1}{T} \qquad 3.23$$

Hence the plot between $\ln\,(e_n/T^2)$ and $1/T$ gives straight line. The slope of this line gives the activation energy of the level[8].

$\ln\left(\frac{e_n}{T^N}\right)$ and $\frac{1}{T}$ where the value of N lies between 1 and 2.

3.3.3. DEEP LEVEL CONCENTRATION :

If we apply reverse bias to a junction Fermi level shifts with respect to the deep levels and electrons are emitted to empty those levels which were filled before the application of reverse bias. Due to emission of electrons the charge in the depletion region changes which will change the capacitance of the junction. This process will continue for a finite time until all the levels above the Fermi level become empty. If the reverse bias is applied for such a long enough time then after a finite time the change in capacitance will be maximum. If we denote this finite time as $t(\infty)$ and maximum change as $\Delta C(\infty)$ then

$$C(\infty) - C(0) = \Delta C(\infty) \qquad 3.24$$

Now using equation

$$\frac{\Delta C}{C} = \frac{N_T}{2N_I} \exp (- e_n t) \qquad 3.25$$

When $t \longrightarrow \infty$ then $e_n = 0$ and $\Delta C = \Delta C_{max}$ and eq. 3.25 can be written as

$$\frac{\Delta C_{max.}}{C} = \frac{N_T}{2N_I} \qquad 3.26$$

$$=> \qquad N_T = \frac{\Delta C_{max.}}{C} \cdot 2N_I \qquad 3.27$$

Where N_I is the shallow level concentration. In case of p^+n, N_I will be N_D. Hence deep level concentration can be found by eq. 3.27 from measured values of $\Delta C_{max.}$, C and N_D.

3.4. DARK CAPACITANCE TRANSIENT TECHNIQUES :

There are many techniques to obtain the current and capacitance transients. One of these techniques is Dark Capacitance Transients technique which is commonly used for its convenience. In this technique the sample is placed in perfect dark conditions. There are three different ways to analyse the behaviour of dark capacitance transients which are discussed below.

3.4.1. SINGLE SHOT CAPACITANCE TRANSIENT TECHNIQUE:

A system in equilibrium or in steady state can be perturbed and then allowed to relax back to its original state. Its relaxation exposes properties of the physical system. When such an experiment is carried out just once or repeated for a few times to improve its accuracy , it is classed as single shot measurement.

Consider a $p^{+}n$ junction at equilibrium as shown in Fig.3.1. The deep levels are filled for $X > W - \lambda$ and empty for $X < W - \lambda$. The abscissa $X = W$ represents the limit of the depleted zone. If we suddenly apply a reverse bias, then the new steady state situation will correspond to Fig. 3.2. There will be a transient region between these two steady states i.e. $W_1 > W$ and $W_1 - \lambda_1 > W - \lambda$. The filled states located in the region $W - \lambda < X < W_1 - \lambda_1$ will emit their electrons to the conduction band. This emission can be obtained by measuring the current which flows through the junction but in our case we measure the change in capacitance of the junction.

Let the charge density in the depleted zone be $\rho(x)$ and also assume that there is an abrupt transition at $X = W$ between the depleted zone and neutrality region. Then the potential drop V across the region is given by

$$V = \int_{0}^{W} X \, \rho(x) \, dx \qquad 3.28$$

Now the stored charge in that region is given by

$$Q = A \int_{0}^{W} \rho(x) \, dx \qquad 3.29$$

Where A is the area of the region. Now the capacitance is given by

$$C = -\frac{dQ}{dV} \qquad 3.30$$

Hence from the equations 3.28 — 3.30 we get

$$C = \frac{\varepsilon A}{W} \qquad 3.31$$

which is the usual capacitance for a plane capacitor. The change in capacitance on application of reverse bias takes place continuously between its two limits W and W_1. Hence the total change in depletion region will be

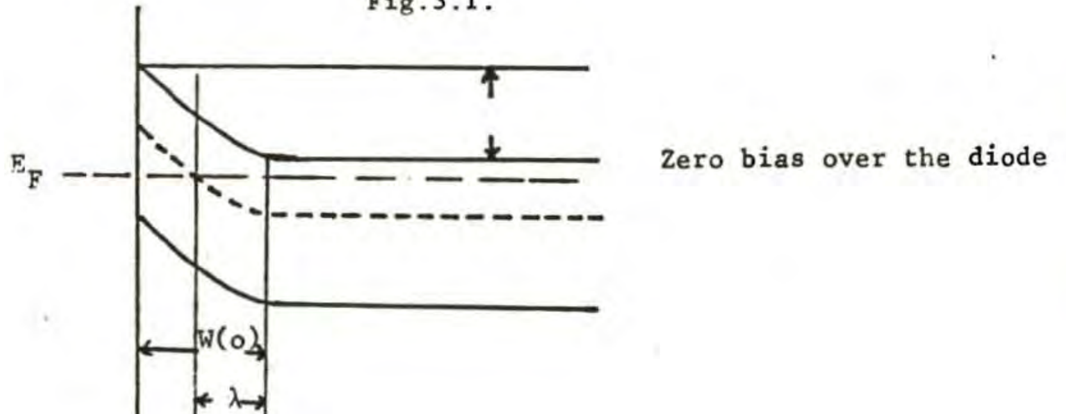
$$\Delta W = W_1 - W$$

Now at any instant we measure the change in depletion region and also assume that the quantity remains small, so that we can write

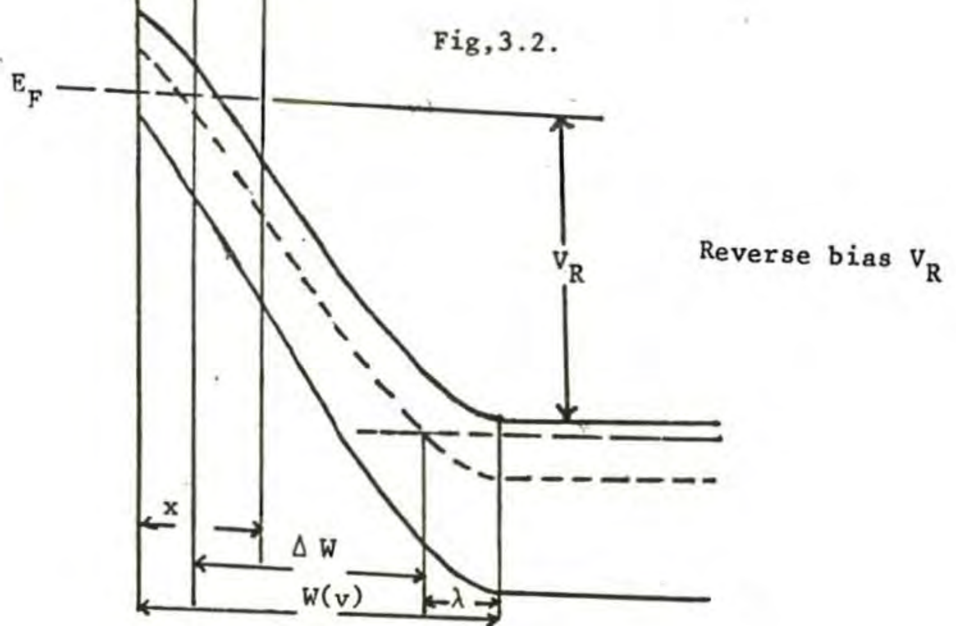
$$\frac{\Delta C(t)}{C} = - \frac{\Delta W(t)}{W_1} \qquad 3.32$$

Since during a full transient the applied potential remains same i.e. V_1, so there is a relation between charge density and depletion width can be obtained by

Fig.3.1.



Fig,3.2.



differentiating the eq.3.28. i.e.

$$0 = W_1 \rho(w_1) \Delta W + \int_0^{w_1} X \Delta\rho(x,t) dx \qquad 3.33$$

$$\Delta W = - \frac{1}{W_1 \rho(w_1)} \int_0^{w_1} X \Delta\rho(x,t) dx \qquad 3.34$$

Combining 3.34. and 3.32. we get

$$\frac{\Delta C}{C} = \frac{1}{W^2 \rho(w_1)} \int_0^{w_1} X \Delta\rho(x,t) dx \qquad 3.35$$

As it is obvious from figures 3.1 & 3.2 the change in charge density depends on the change of the concentration of filled traps i.e.

$$\Delta\rho(x,t) = - q \Delta n_T \qquad 3.36$$

If f_0 denotes the Fermi Dirac distribution when applied bias is zero and f_1 for applied bias is V_1, then $f_0 - f_1$ represents the initial perturbation with respect to f_1. If $W_1 - \lambda_1 - (W - \lambda)$ is sufficiently large compared to the width of the Fermi distribution then $f_1 - f_0$ can be approximated by 1 in this interval and zero outside this interval. By using eq.

$$f(t) - f(\infty) = (f(0) - f(\infty)) \exp\left[- \frac{e_n t}{1 - f(\infty)}\right]$$

Putting $f_{(0)} = f_1 = 1$ & $f(\infty) = 0$, finally we can write

$$f(t) = \exp\left(- \frac{t}{\tau}\right) \qquad 3.37$$

And this gives

$$\Delta\rho(x,t) = - qN_T \exp(- \frac{t}{\tau}) \qquad 3.38$$

Hence we can write

$$\frac{\Delta C}{C} = \frac{N_T}{2N_D} \frac{(W_1 - \lambda_1)^2 - (W - \lambda)^2}{2} \exp(-\frac{t}{\tau}) \qquad 3.39$$

If λ and λ_1 are much smaller than W and W_1, then eq.3.39 becomes

$$\frac{\Delta C}{C} = \frac{N_T}{2N_D} \frac{W_1^2 - W^2}{2} \exp(-\frac{t}{\tau}) \qquad 3.40$$

If λ and λ_1 have significant values then we cannot neglect them and this is termed as edge effect. Practically $V_R >> V_B$ so $W_1 >> W$ and hence eq. 3.40 can be written as

$$\frac{\Delta C}{C} = \frac{N_T}{2N_D} \exp(-\frac{t}{\tau}) \qquad 3.41$$

$$=> \qquad \Delta C = C \frac{N_T}{2N_D} \exp(-\frac{t}{\tau})$$

Taking natural log on both sides we get

$$\ln \Delta C = -\frac{1}{\tau} t + \ln \frac{C N_T}{2 N_D} \qquad 3.42$$

This is an equation of a straight line. The slope of the equation gives the emission rate. For holes the same procedure is used with convenient changes in parameters.

3.4.2 THERALLY STIMULATED CAPACITANCE TECHNIQUE:

Thermally Stimulated Capacitance (T.S.Cap.) method is convenient for studying the high temperature annealing properties of lattice defects. This method provides information about two parameters of the lattice defects, thermal activation energy $\Delta E_{n,p}$ and trap concentration N_T, very quickly.

In this method, the sample is mounted in a cryostat and is excited by illumination, by forward biasing or zero

biasing to a non-equilibrium state of the traps. The device is first cooled to attain a low temperature. The low temperature is selected such that the thermal emission rates of the traps, present in the device, should be insignificant at this temperature. After filling the traps, the temperature is raised at a linear rate and the junction capacitance is monitored as a function of tempera The same procedure is repeated for the same sample with-out initial excitation of carriers. Comparison of the two scans reveals the presence of deep levels which tend to empty at some particular temperature showing capacitance step.

3.4.3. DEEP LEVEL TRANSIENT SPECTROSCOPY:

Deep Level Transient Spectroscopy is an efficient method of evaluating some of the important parameters of deep level impurities in semiconductors. The method was originally suggested by D.V.Lang (1974)[9]. When the bias of the diode is abruptly changed, the capacitance also changes abruptly. Following the abrupt capacitance change, an exponential or multi-exponential transient can often be found, which originates from the deep level impurities in the material. The merit of DLTS is that the time constant and the amplitude of this transient are evaluated in a natural way. It allows to some extent an easy separation of various emission rates occurring in the same temperature range.

In this technique periodical filling pulses are applied on a reverse biased junction. The analysis of resultant transient is performed using a filtering operation. The transient capacitance resulting from the filling pulses

has the form

$$\Delta C(t) = - \Delta C_o \exp(- \frac{t}{\tau}) \qquad 3.43$$

The time constant of the transient can be obtained by taking the derivative of the signal at a given time t_o.

$$\frac{d\Delta C}{dt} = \frac{\Delta C_o}{\tau} \exp (- \frac{t_o}{\tau}) \qquad 3.44$$

When the temperature T varies emission rate $e_n = \frac{1}{\tau}$ varies accordingly and $\left[\frac{d\Delta C}{dt} \right]_{t_o}$ goes through a maximum for T_o such that $t_o = \tau$ since

$$\frac{d}{de_n} \left[\frac{d\Delta C}{dt}\right]_{t_o} = \Delta C \left[1- \frac{t_o}{\tau} \right] \exp\left[- \frac{t_o}{\tau} \right] \qquad 3.45$$

Thus fixing t_o is equivalent to the selection of a given value '$e_n(t_o)$' of the emission rate. The temperature T_o at which the maximum of the derivative occurs, corresponds to $e_n(t_o) = \frac{1}{\tau_o}$. In practice the derivative of the signal $\Delta C(t)$ is obtained by fixing the difference $\Delta C(t_1) - \Delta C(t_2)$ of the amplitude at two times t_1 and t_2 measured with the help of a double boxcar.

Generally DLTS analysis is a filter operation. The measuring system gives a non-zero signal when emission rate is situated in given window as shown in Fig. 3.3.
The filter, described above

$$f(t) = \delta(t-t_1) - \delta(t-t_2) \qquad 3.46$$

provides the following response.

$$R(e_n) = S_o \left[\exp\left(- \frac{t_1}{\tau} \right) - \exp\left(- \frac{t_2}{\tau} \right)\right] \qquad 3.47$$

which is maximum for

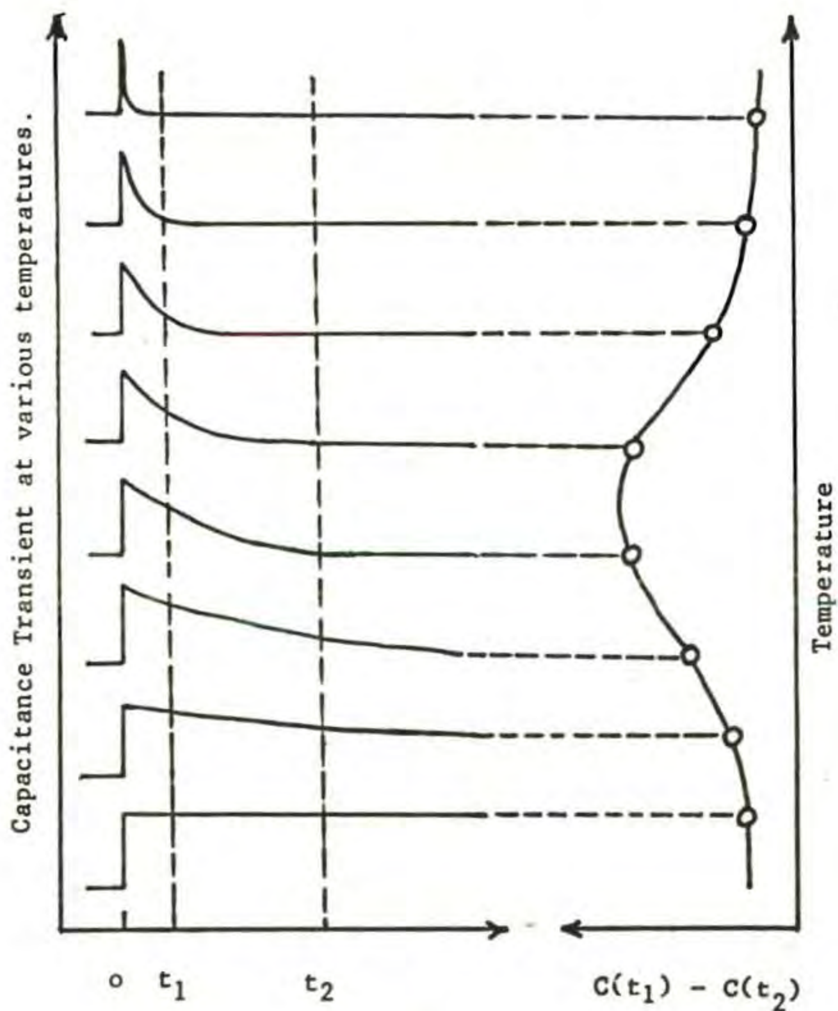


Fig. 3.3.

$$e_n = \frac{\ln(\frac{t_1}{t_2})}{t_2 - t_1} \qquad 3.48$$

We can influence the time window by changing the positions of the gates t_1 and t_2. In principle we can change the time window in three different ways.

1. Fixing t_1 and varying t_2.
2. Fixing t_2 and varying t_1.
3. Fixing $\frac{t_1}{t_2}$ and vary both t_1 and t_2.

The most convenient is to keep the ratio constant, and both shape and amplitude will be independent of τ_{max}.

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CHAPTER 4

EXPERIMENTAL DETAILES

4.1. DEVICES :

The devices used in this work were $p^{+}n$ green light emitting diodes (LED's). These devices were prepared by zinc diffusion in nitrogen doped n-type liquid-phase-epitaxial (LPE) GaP by Ferranti ltd.(U.K).The devices had an area of $0.5 \times 0.5\ mm^2$ and had been epoxy encapsulated after providing suitable ohmic contact leads. The C-V measurements on the test diodes revealed that the junctions were abrupt (see next section). The devices used had zero bias capacitance of 134 pF to 144 pF at room temperature.

4.2. C - V MEASUREMENTS :

To characterise the deep level contents of a diode it is necessary to have information about its shallow level concentration. It is also necessary to know the built-in potential. The capacitance-voltage characteristics of a diode provide such information about it. The C-V plot gives the following information.

i. Type of the junction.

ii. Built in voltage.

iii. concentration of the Shallow dopants.

For a step junction p^+n diode

$$\frac{1}{C^2} = \frac{2}{A^2 \varepsilon_o \varepsilon_r q (N_D - N_A)} (V_R + V_B) \qquad 4.1$$

Where C denotes the capacitance, A is area, q is electron charge, ε_o is the permativity of free space and ε_r is the relative permativity of the material, N_D and N_A represent the shallow dopant donor and accepter respectively. V_R and V_B represent the applied reverse bias and built-in voltage. The linear relationship between $\frac{1}{C^2}$ and V_R implies that a junction is step junction if a straight line is obtained on plotting $\frac{1}{C^2}$ versus V_R. On extrapolation of the straight line the x-intercept gives the value of the built-in voltage. From the slope of this straight line one can calculate the shallow level dopant concentration by using the formula:

$$\text{Slope} = \frac{2}{A^2 \varepsilon_r \varepsilon_o q (N_D - N_A)} \qquad 4.2$$

Similarly for a linearly graded junction[1];

$$\frac{1}{C^3} = \frac{12}{A^3 \varepsilon_r^2 \varepsilon_o^2 q a} (V_R + V_B) \qquad 4.3$$

where a is the concentration gradient. Hence if $\frac{1}{C^3}$ versus V_R plot gives a straight line, then the junction is linearly graded.

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1. C. VAN OPDORP : Capacitance-Voltage Relations of Schottkyand p-n diodes, Phy. stat sol. 32,81(1969)

4.3. TEMPERATURE CONTROL SYSTEM :

In single shot measurements the stability of the temperature is utmost important. It was observed that for the diodes on which the present measurements were made a change of one degree in sample temperature changed the junction capaci- tance by about 0.01 pF. Since the total measured change in capacitance is nearly 1pF, the stability of the temperature became all the more important. The system used to minimise the change in temperature consisted upon a home built cryostat with an electronic temperature controller Unipan type 650. In the cryostat the sample was mounted on a copper strip which was thermally isolated from body of the cryostat by using asbestos sheet. On one side of the strip a resistive heater was mounted and on the other side the sample was placed in such a way that the head of the sample touched the strip and the terminals were connected to the capacitance meter. A platinum sensor type 2100 s was connected to the temperature controller. This setup minimised the change in temperature up to $\pm$ 0.025 $^{\circ}$K.

4.4. SINGLE SHOT MEASUREMENTS :

The block diagram of experimental set up is shown in Fig 4.1. A Boonton 72-B capacitance meter was used for capacitance measurements. The test signal (ΔV_{osc}) for the measurement of capacitance in this meter is of high frequency

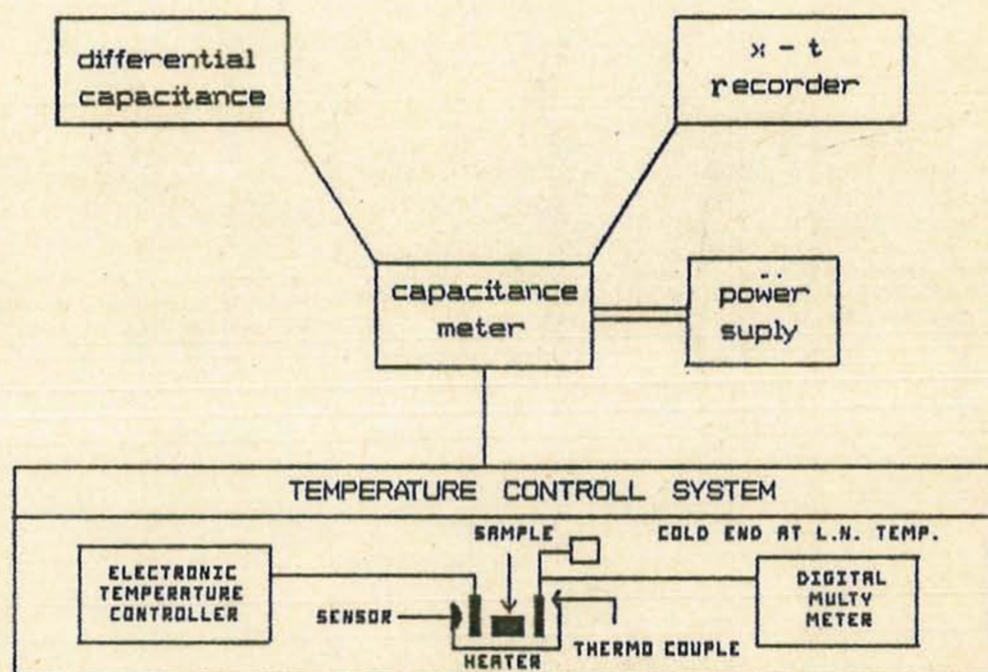


Fig. 4.1.

Illustration of the blok diagram of the Single Shot Experimental set up

(1M hertz) and low magnitude (10mV) which fulfils the required conditions for the dark transient capacitance experiments. The capacitance meter is capable of measuring differential capacitance i.e. a small change in capacitance of the test device with respect to a known standard capacitance. A Boonton precision decade capacitor model 76-3A was used as variable standard back-off capacitance. The output capacitance signal was recorded on an x-t recorder PL-3 (J J Instruments). The system provides a maximum resolution of $5x10^{-5}$ pF.

For the single-shot capacitance transient measurements the stability of the sample temperature is of utmost importance. This was achieved by using the set-up described above in section 4.3. The D.C. step voltages were applied using a Philips D.C. power supply PE-1514, connected with a well shielded switch operated manually. The power supply could be used for any step voltage from 0 to 20 volts. The transients were obtained by switching the junction diode bias from zero to reverse typically 5 to 7 volts.

4.5. DEEP LEVEL TRANSIENT SPECTROSCOPY MEASUREMENTS :

The theory of deep level transient spectroscopy (DLTS) was detailed in section 3.4.3. The present DLTS measurements were carried out using a Metrimpex DLS-81 deep level spectrometer based on the lock-in-principle. The samples were mounted in variable temperature cryostat with a copper

constantan thermocouple mounted symmetrically with respect to the sample to monitor the temperature. Temperature accuracy better than one degree could be attained with this set-up. Excitation of the deep levels was performed using the usual reduced reverse bias majority carrier pulses.

The DLTS technique gives the emission rate data with in two-three orders of magnitude for most practical set-ups. In case of the presently investigated mid gap level this range was limited to about one order of magnitude due to the prohibitively high temperatures involved for higher rate windows . The highest emission rate window used on this level is 2.26 sec^{-1} which gave a DLTS peak at 475 K which is just about the highest advisable temperature for safe measurements . The lowest practical emission rate window allowed by the DLTS for this level is 0.1 sec^{-1} which means that one could only obtain the DLTS spectra for the mid gap level over a decade of emission rates.

CHAPTER NO. 5

RESULTS AND DISCUSSIONS

5.1. C - V MEASUREMENTS :

The experimental procedure is explained in sec. 4.2.1. The applied reverse voltage was within the range of 0 volt to 7 volts. The corresponding change in capacitance measured by the Boonton 72-B capacitance meter was ploted on a graph paper i.e. $\frac{1}{C^2}$ along y-axis and applied reverse bias along X-axis. Such C - V plots for diodes E-112-II and AM 325-V are shown in Figs. 5.1 and 5.2 respectively. These plots show that the diodes were step junctions. The Shallow level concentration was found to be 2.66×10^{17} and 1.11×10^{17} and built in potential was 2.1 volts and 1.9 volts respectively.

The C-V characteristics of the third diode were similar.

5.2. SINGLE SHOT MEASUREMENTS :

For single shot measurements, as explained in section 4.2 , after attaining a steady temperature T, the bias on the diode was changed from 0 to V_R (-5 volts for two diodes and -7 volts for the third diode). The corrosponding change in junction capacitance was recorded on the x-t recorder A

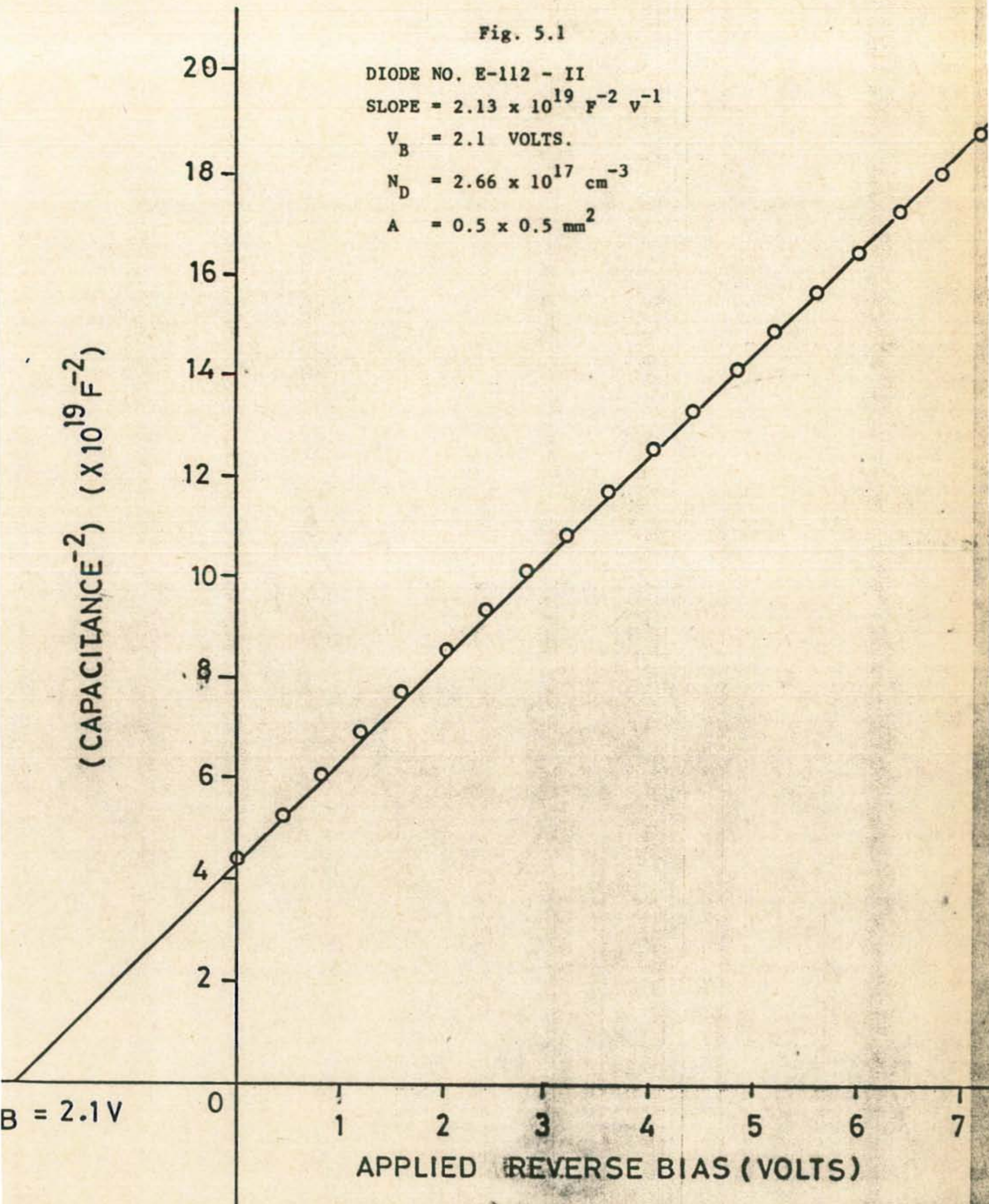


Fig. 5.1
DIODE NO. E-112 - II
SLOPE = 2.13 x 10^19 F^-2 V^-1
V_B = 2.1 VOLTS.
N_D = 2.66 x 10^17 cm^-3
A = 0.5 x 0.5 mm^2
(CAPACITANCE^-2) (X 10^19 F^-2)
APPLIED REVERSE BIAS (VOLTS)
B = 2.1 V
0
1
2
3
4
5
6
7
2
4
6
8
10
12
14
16
18
20

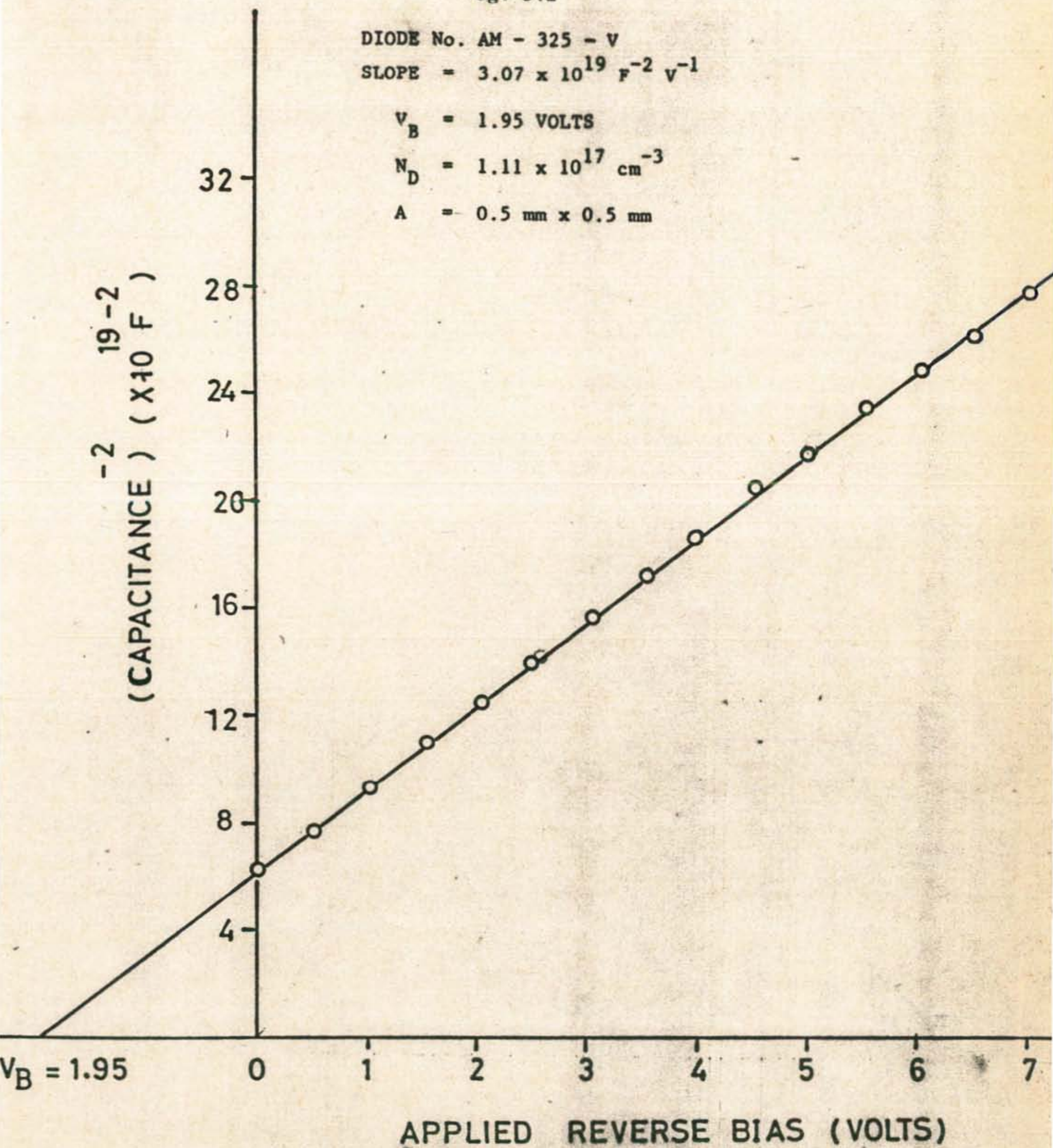


Fig. 5.2
DIODE No. AM - 325 - V
SLOPE = 3.07 x 10^19 F^-2 V^-1
V_B = 1.95 VOLTS
N_D = 1.11 x 10^17 cm^-3
A = 0.5 mm x 0.5 mm
(CAPACITANCE^-2) (X10^19 F^-2)
32
28
24
20
16
12
8
4
V_B = 1.95
0
1
2
3
4
5
6
7
APPLIED REVERSE BIAS (VOLTS)

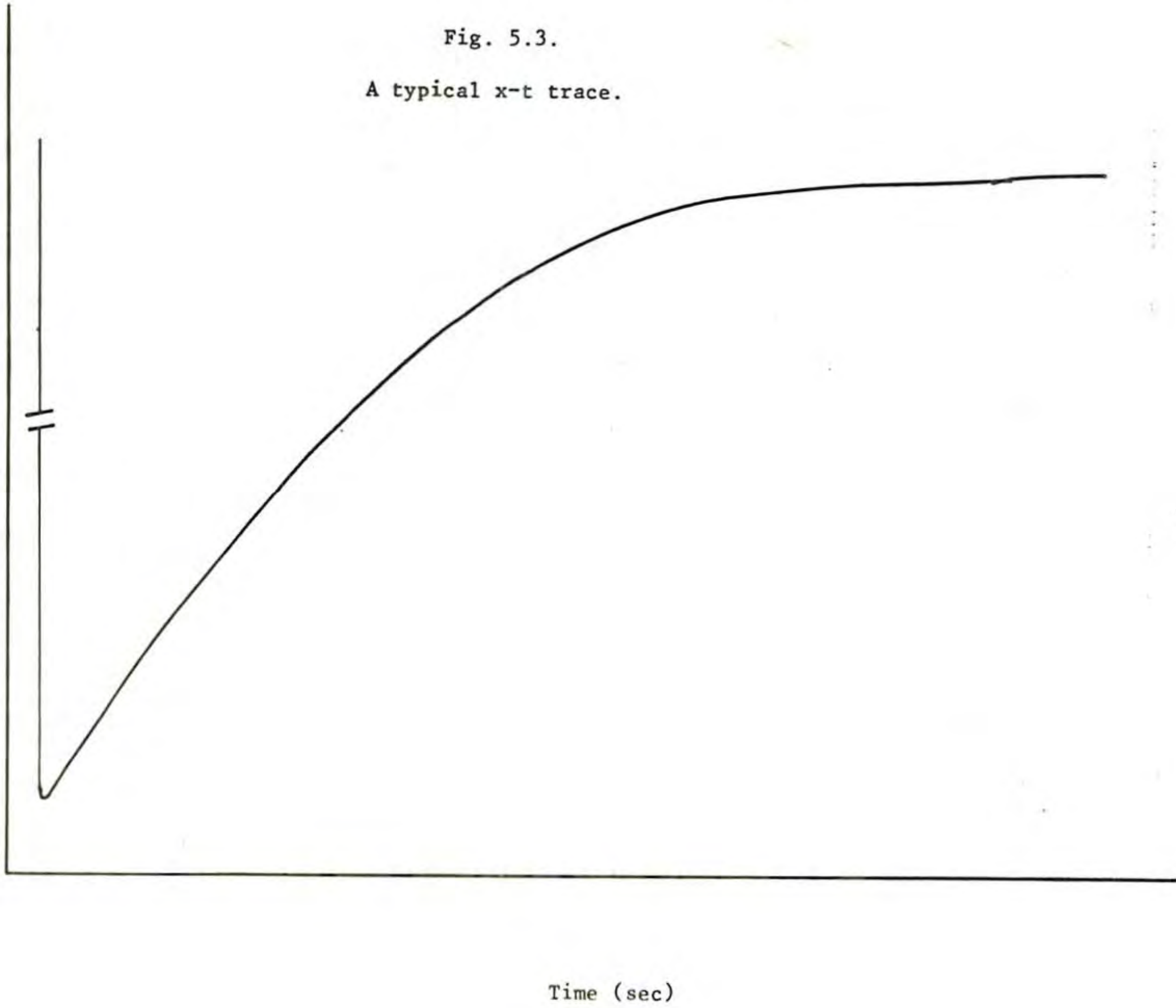


Fig. 5.3.
A typical x-t trace.

On application of the step bias to the junction the capacitance first fell sharply and then an increasing transient followed. The time dependent change in capacitance is understood in terms of emission of electrons/holes from deep levels in the depletion region as explained in section 3.4.1.

The initial sharp fall of capacitance can be explained in terms of emission of holes from hole-traps on n-side of the junction or the emission of electrons from electron traps from p-side of the junction . As the sample used were p^+n junctions , in which almost the entire depletion region lies on the n-side of the junction , so this fall in capacitance had to be due to the emission of holes from hole levels on the n-side of the junction. The temperature used in these measurements was very high, at these temperatures this falling transient had duration of a few seconds and the response time of the recorder is also a few seconds so it was impossible to get accurate measurements in this time range. The origin of this falling transient is understood well in terms of hole emission from the 0.85 eV level[1]. So this part of the transient was neglected.

The rising transient is due to the emission of electrons from the electron levels on the n-side of the junction (majority carriers). The rising transints obtained from the x-t recorder were ploted on log-linear scale (change in capacitance along log scale and time on linear scale). Typical transients at three temperatures from each test

diode, are shown in Figs. 5.4 to 5.12.

It is clear from these Figures that the transients are non exponential, in general describable as sum of two exponentials. This suggests electron emission from two distinct levels at these temperatures.

I. SECOND (SLOWER) PART OF THE TRANSIENT:

The emission rates obtained from this part are tabulated in Tables 5.1 to 5.3 for the three test diodes. The emission rate data obtained from these plots were ploted against the inverse of temperature giving the Arrhenius plots. These Arrhenius plots are showen in Figures 5.13, 5.14 and 5.15. The slope of arrhenius plots give the energy of the trap level according to equation 3.23. The energies obtained from these Arrhenius plots are given in the table 5.4. The average energy is $E_T = 1.03 \pm 0.02$ eV. Thus this part of the transient is due to electron emission from the level situated at $E_C - E_T = 1.03 \pm 0.02$ eV, where E_C is the energy of the conduction band minimum and E_T is the energy of the trap level.

II. FIRST (FASTER) PART OF THE TRANSIENT:

The first part of the transient is effected by the second (slower) part and had to be corrected. For this purpose the long time exponential part was extrapolated to small time region. Then for each data point in the first region the ΔC values corrosponding to the extrapolated line were subtracted from the observed values. This procedure and the corrected ΔC values (triangles) are also plotted in Figs. 5.4 to 5.12. The slopes of these corrected lines give the

Fig. 5.4.

Semi-log plot of the dark capacitance transient of diode E-112-III, at T = 356.04 □ for observed and Δ for corrected data.

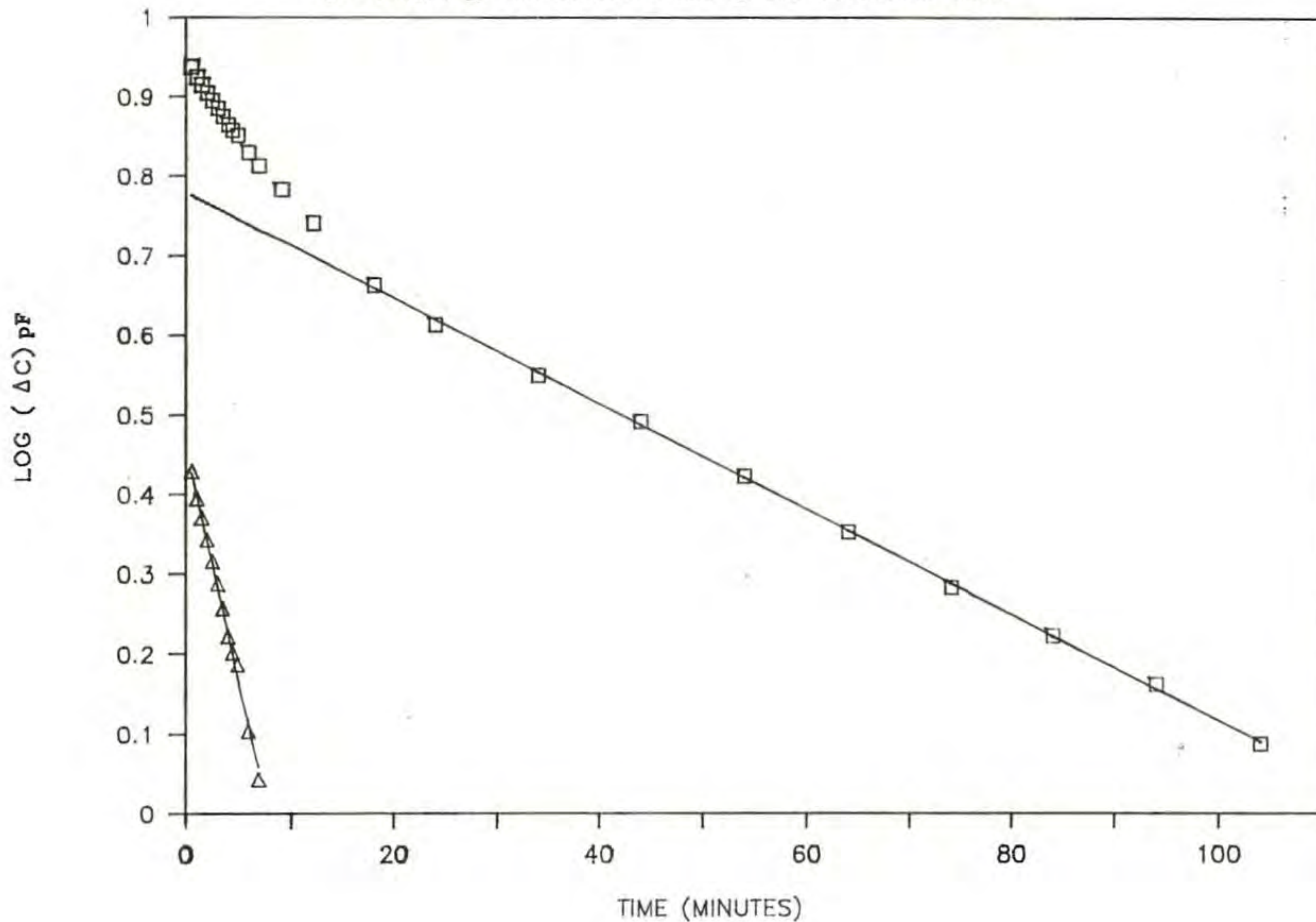


Fig. 5.5.

Semi-log plot of the dark capacitance transient of diode E-112-III at T = 380.43 □ for observed and Δ for corrected data.

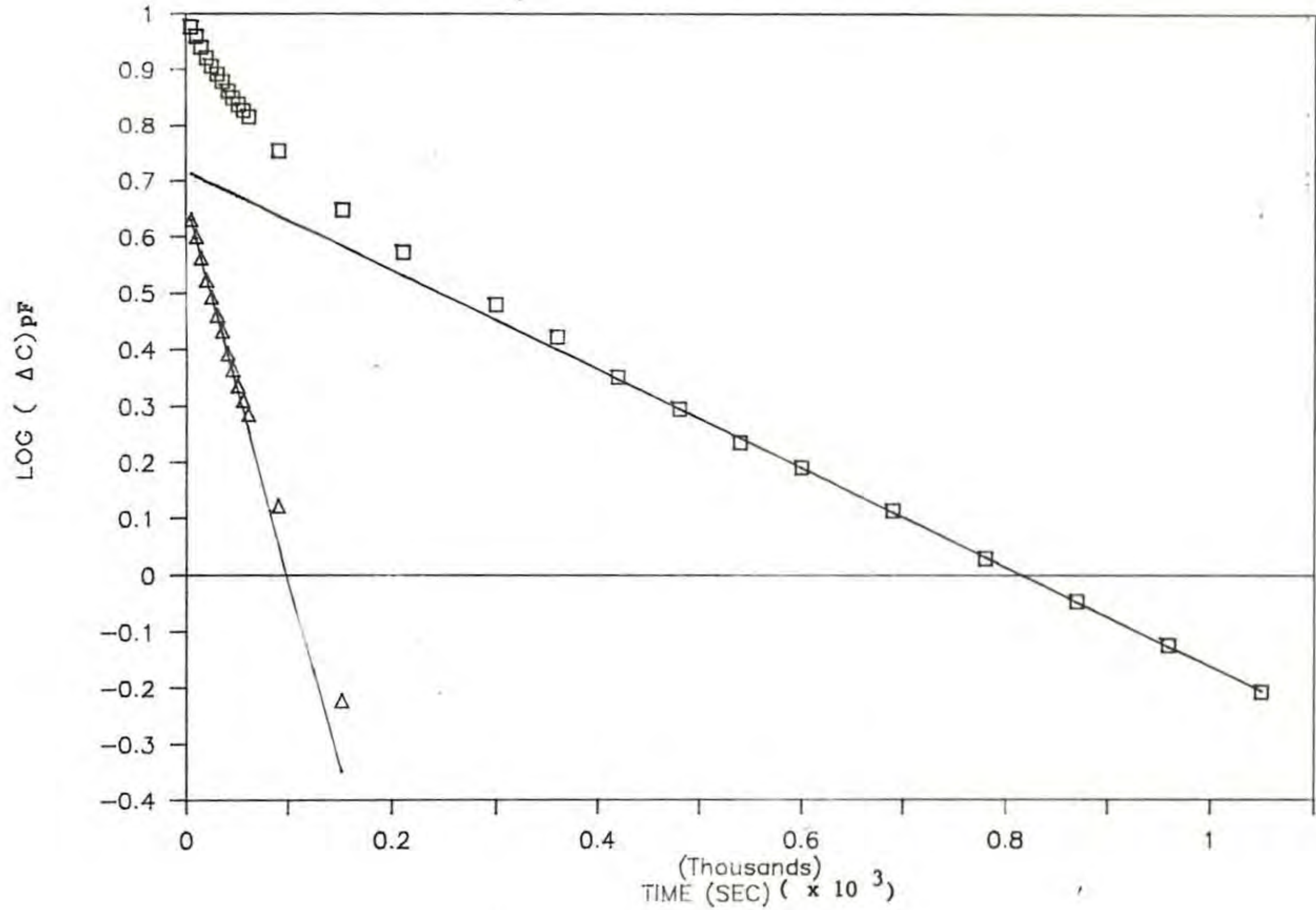


Fig. 5.6.

Semi-log plot of the dark capacitance transient of diode E-112-III at T= 409.2

□ for observed and Δ for corrected data.

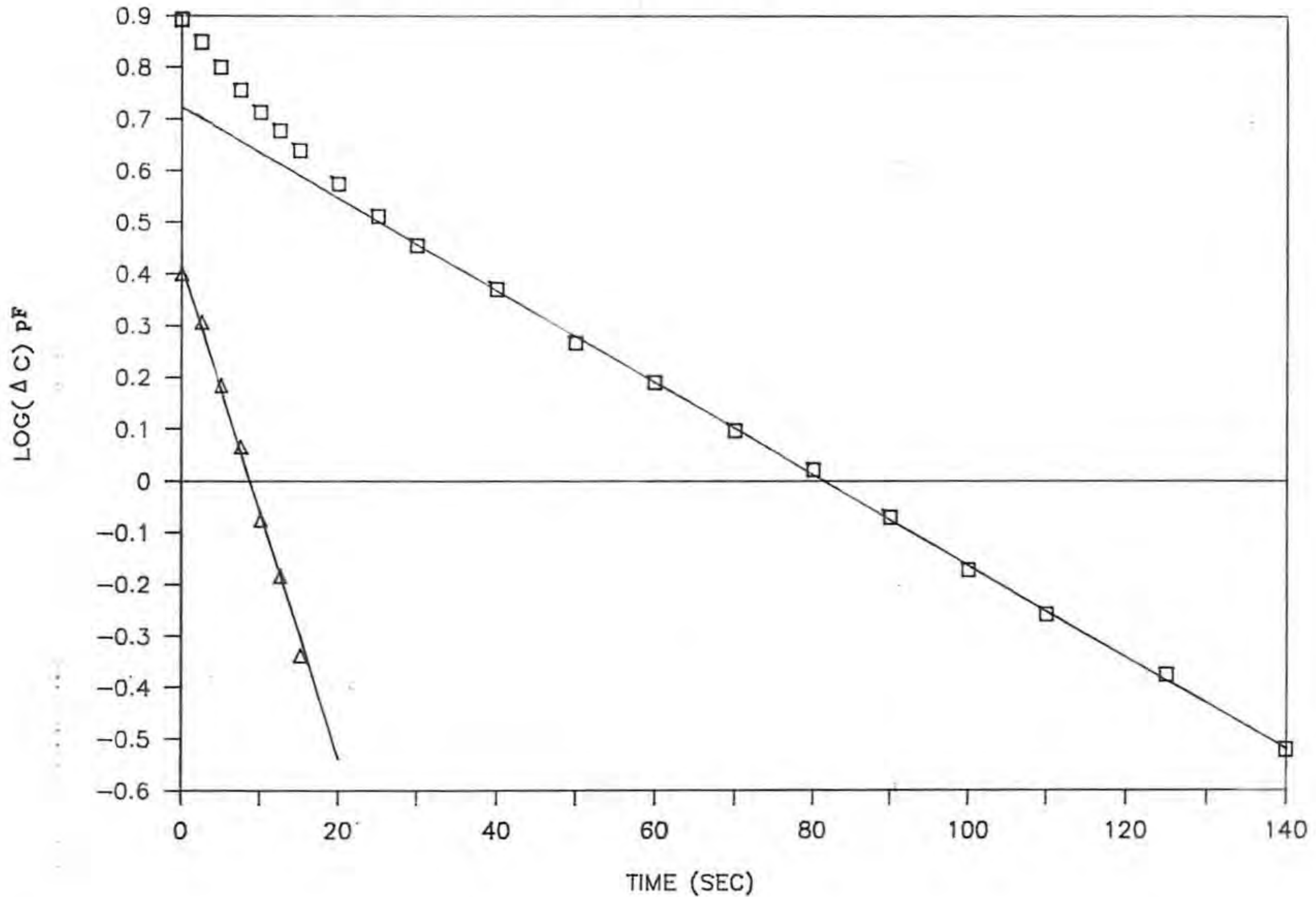
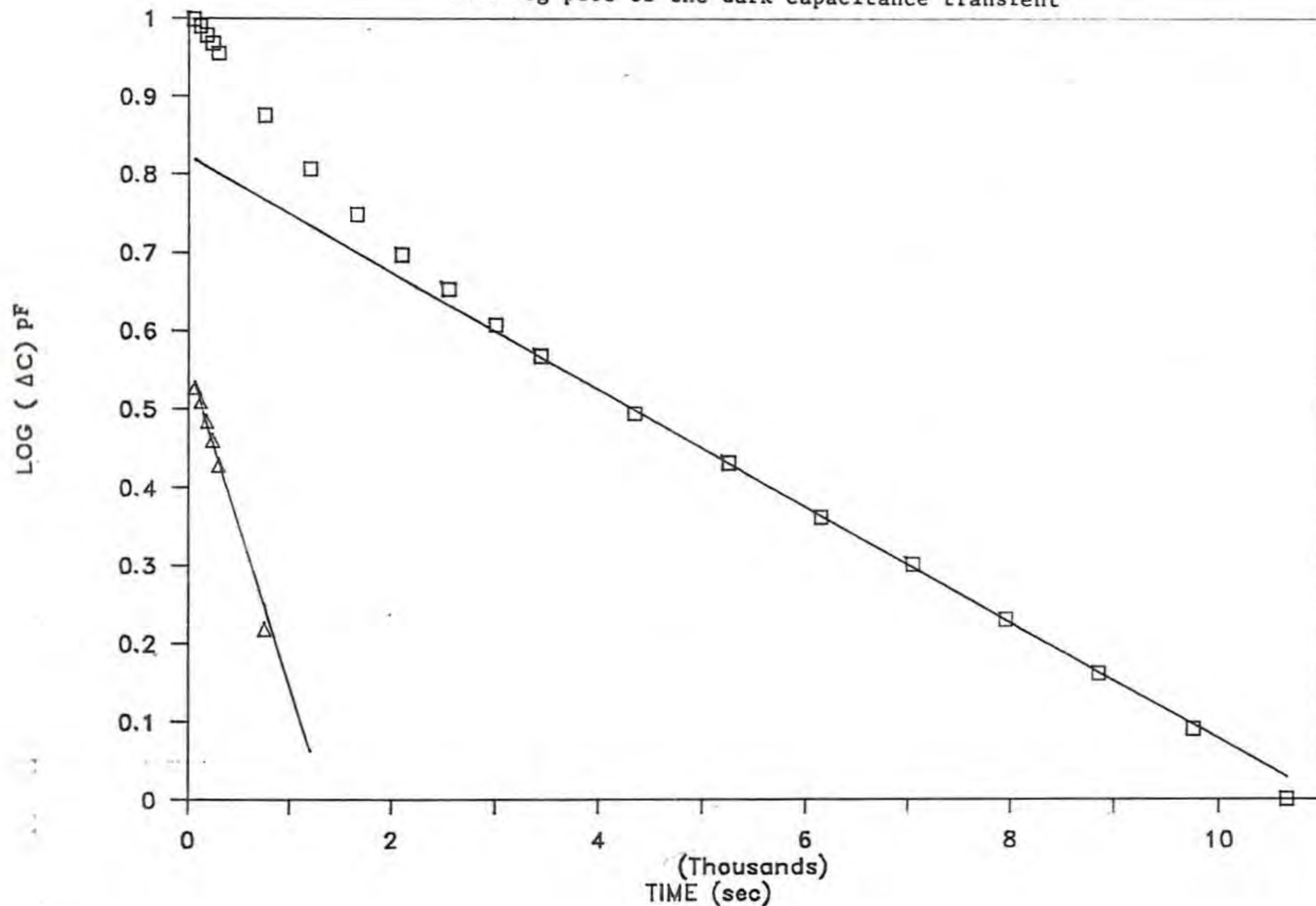


Fig.5.7. Diode # E-112-II T=347.88



- 67 -

Fig. 5.8.

Semi-log plot of the dark capacitance transient of diode E-112-II at T = 382.36 □ for observed and Δ for corrected data.

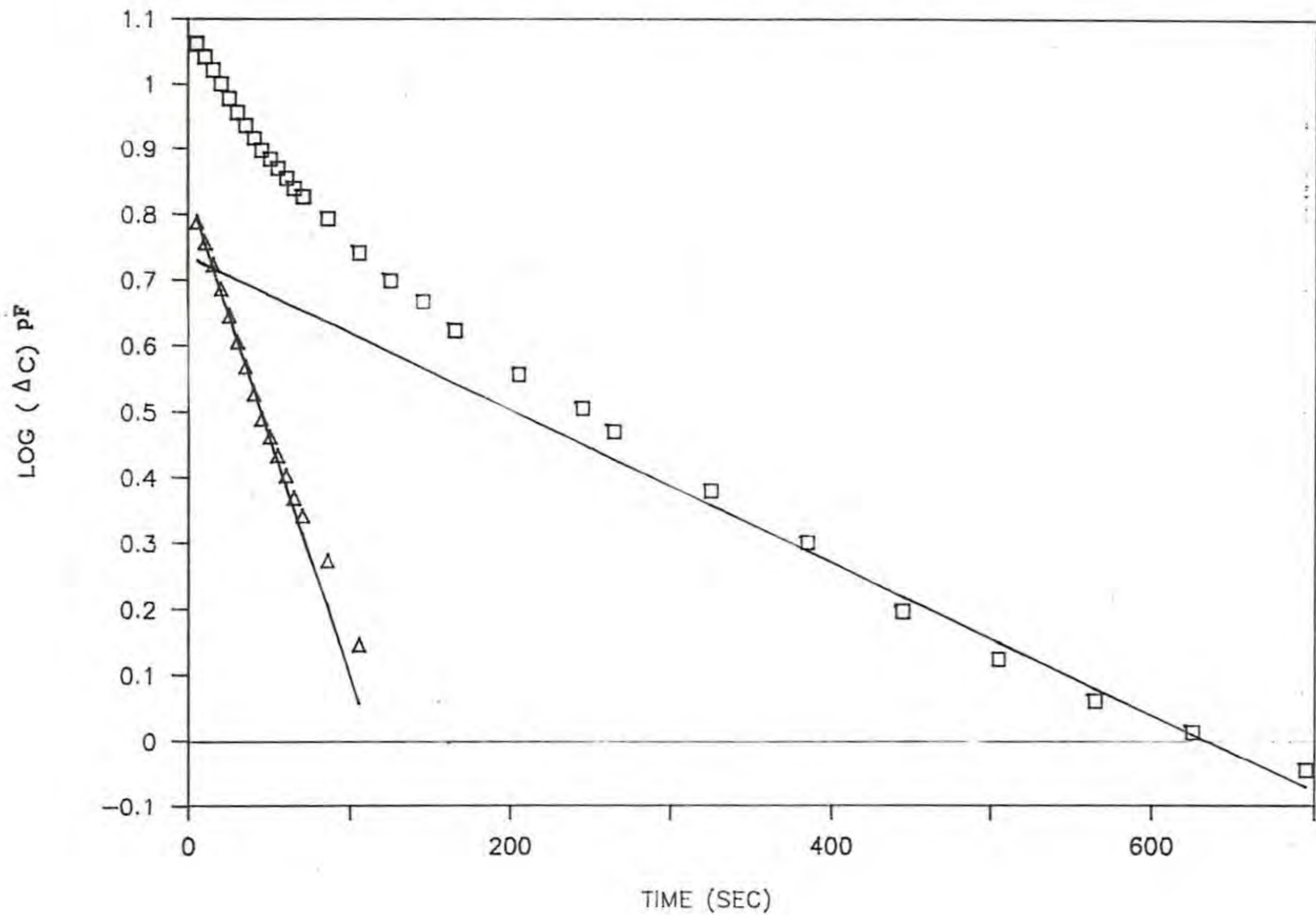


Fig. 5.9.

Semi-log plot of the dark capacitance transient of diode E-112-II at T = 427.7 □ for observed and Δ for corrected data.

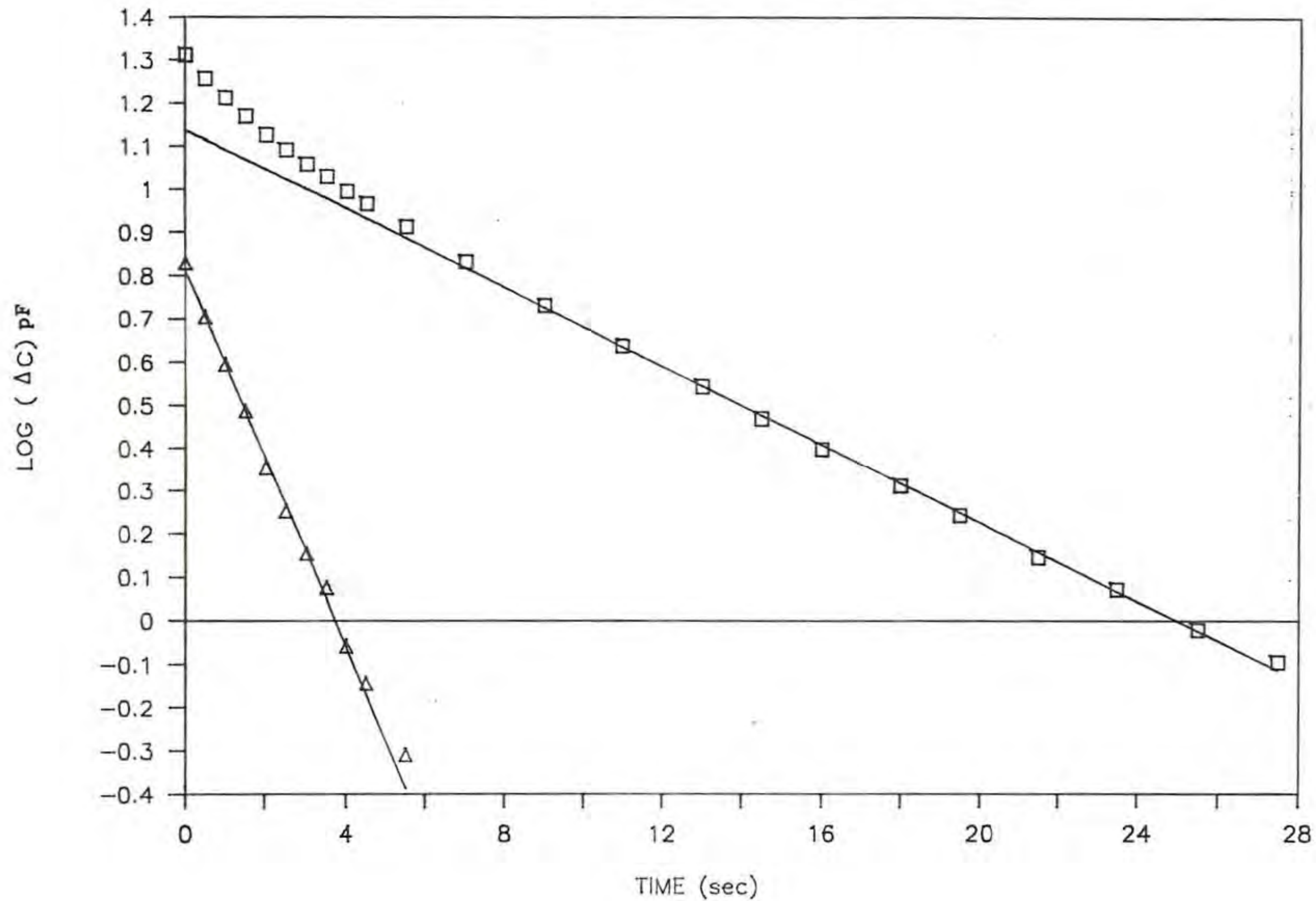


Fig. 5.10. Diode # AM-325-V T=339.8

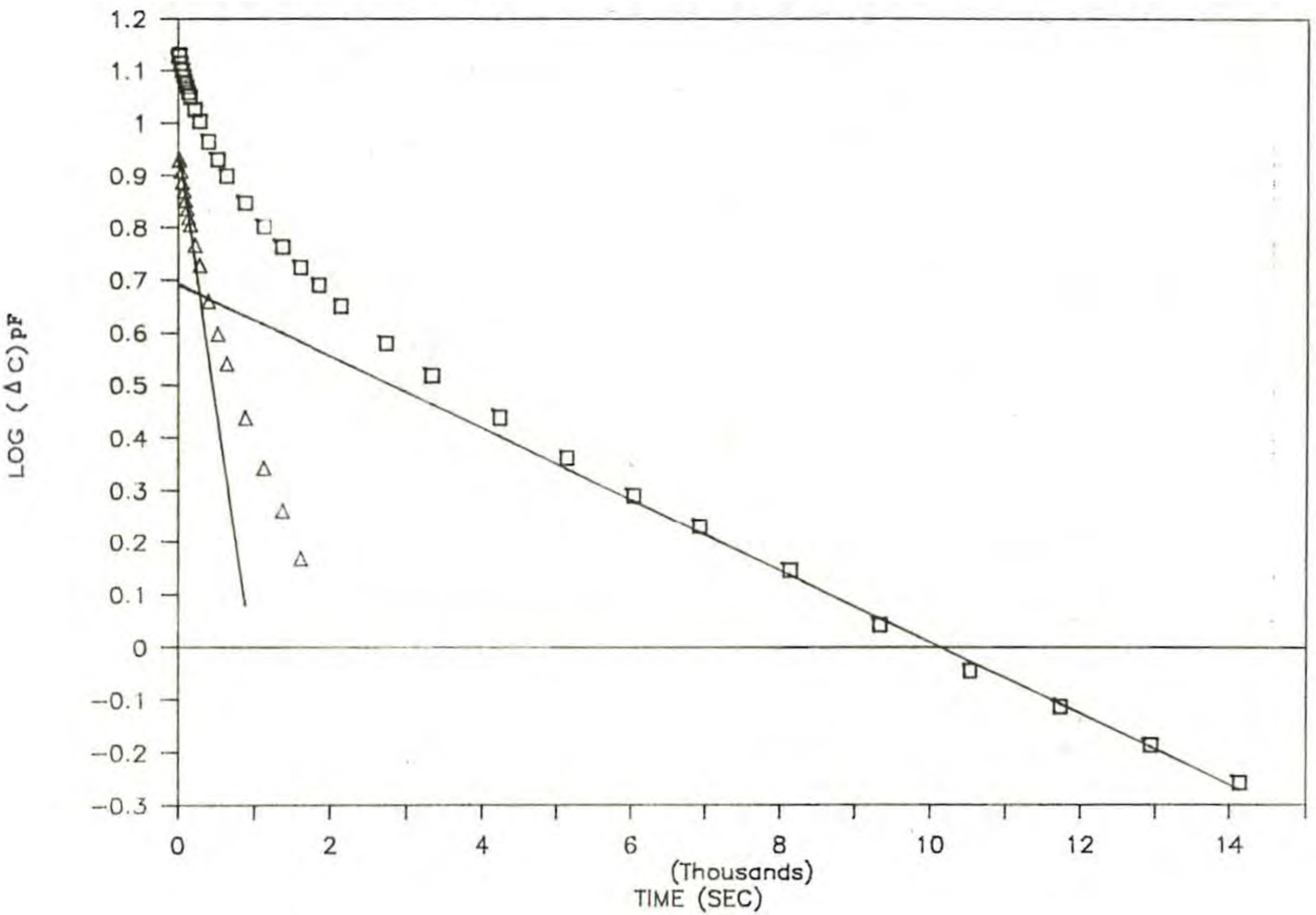


Fig. 5.11. Diode # AM-325-V T=386.88

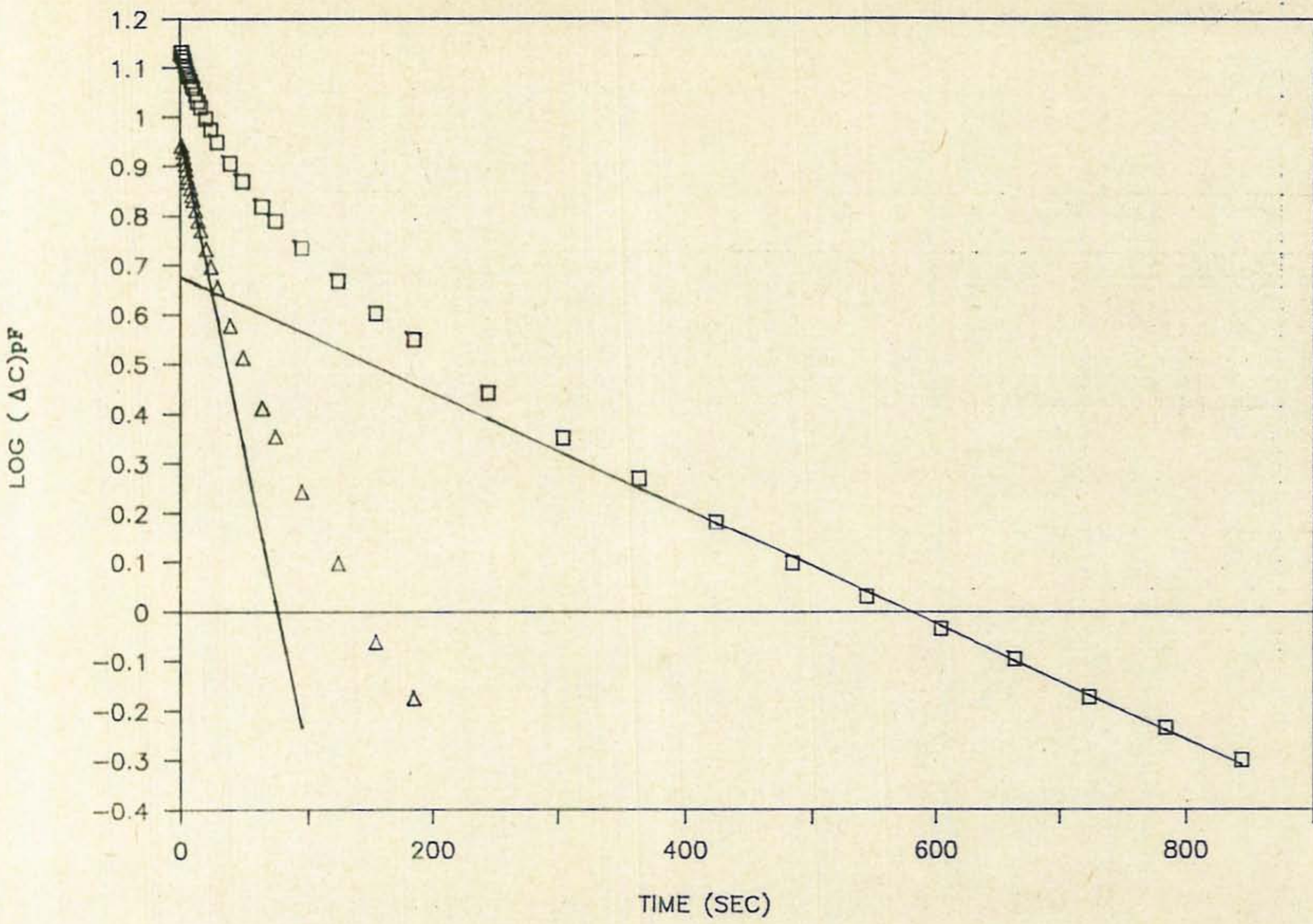


Fig. 5.12. Diode # AM-325-V T=417.22

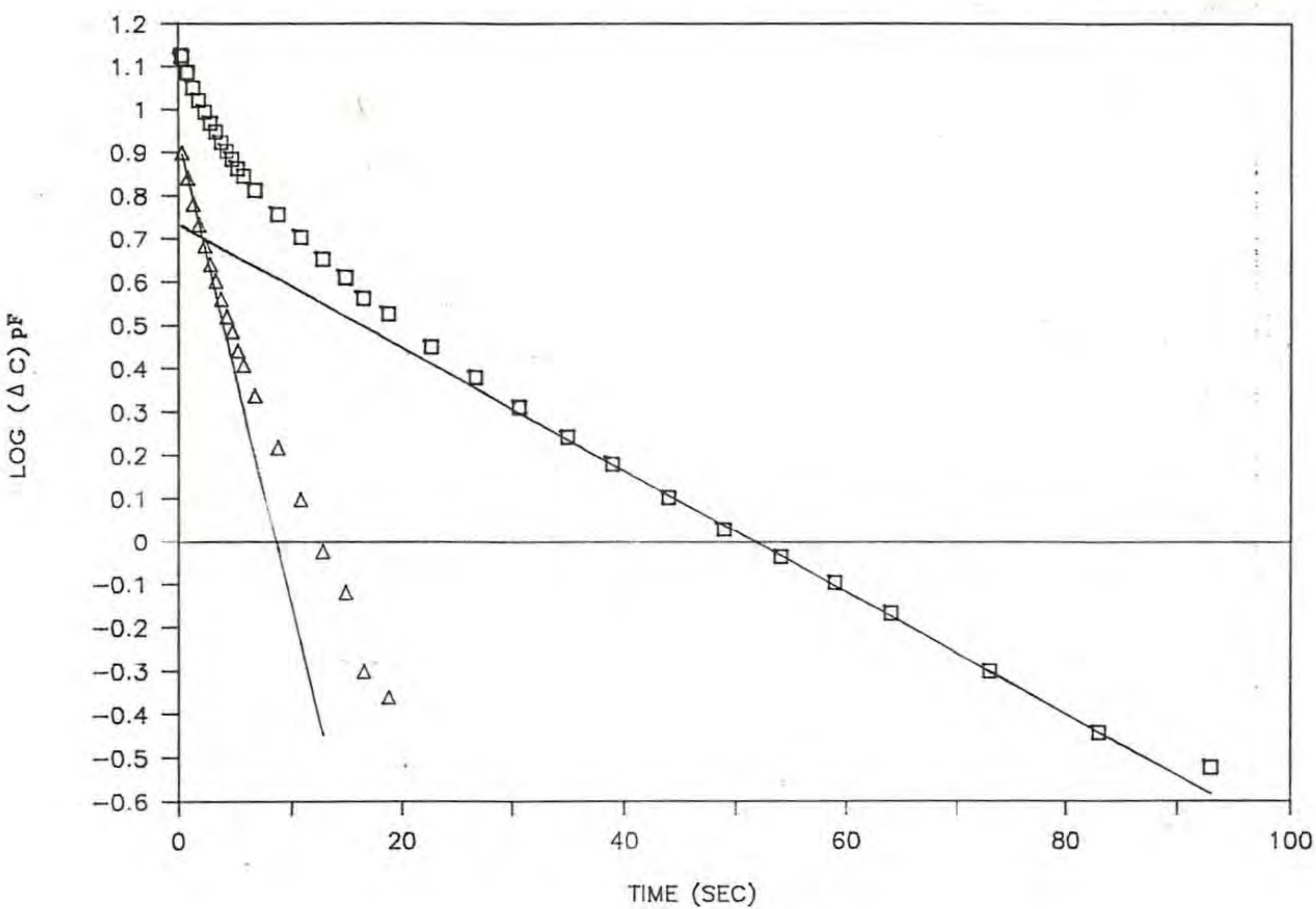


TABLE 5.1

Emission Rate Data for (slower part Transient) of

Diode # E-112-III

S/No.	TEMPERATURE K	EMISSION RATE (Slower Part) sec^{-1}	e_z/T^2 sec^{-1} K^{-2}
1	432.360	1.07×10^{-1}	5.75×10^{-7}
2	421.788	5.06×10^{-2}	2.84×10^{-7}
3	409.196	2.06×10^{-2}	1.23×10^{-7}
4	400.053	9.14×10^{-3}	5.71×10^{-8}
5.	396.592	6.67×10^{-3}	4.24×10^{-8}
6	392.112	5.04×10^{-3}	3.28×10^{-8}
7	383.645	2.50×10^{-3}	1.70×10^{-8}
8	380.717	2.01×10^{-3}	1.38×10^{-8}
9	371.902	8.76×10^{-4}	6.33×10^{-9}
10	362.177	4.56×10^{-4}	3.48×10^{-9}
11	355.231	2.16×10^{-4}	1.71×10^{-9}

TABLE 5.2

Emission Rate Data for (slower part Transient) of

Diode # E-112-II

S/No.	TEMPERATURE K	EMISSION RATE (Slower Part) sec^{-1}	e_2/T^2 sec^{-1} K^{-2}
1	427.704	1.04×10^{-1}	5.69×10^{-7}
2	413.880	4.03×10^{-2}	2.35×10^{-7}
3	408.722	2.25×10^{-2}	1.35×10^{-7}
4	398.282	1.24×10^{-2}	7.85×10^{-8}
5.	390.128	5.00×10^{-3}	3.29×10^{-8}
6	382.360	2.77×10^{-3}	1.89×10^{-8}
7	380.025	2.21×10^{-3}	1.53×10^{-8}
8	370.510	9.22×10^{-4}	6.72×10^{-9}
9	362.717	5.94×10^{-4}	4.51×10^{-9}
10	351.500	2.02×10^{-4}	1.63×10^{-9}
11	347.885	1.77×10^{-4}	1.46×10^{-9}
12	344.750	1.02×10^{-4}	8.58×10^{-10}
13	338.920	7.70×10^{-5}	6.70×10^{-10}

TABLE 5.3

Emission Rate Data for (Slower part Transient) of

Diode # AM-325-V

S/No.	TEMPERATURE K	EMISSION RATE (Corrected Part) Sec^{-1}	e_z/T^2 $Sec^{-1}\ K^{-2}$
1	421.098	4.48×10^{-2}	2.53×10^{-7}
2	417.217	3.26×10^{-2}	1.87×10^{-7}
3	412.878	2.17×10^{-2}	1.27×10^{-7}
4	408.805	1.82×10^{-2}	1.09×10^{-7}
5.	405.103	1.10×10^{-2}	6.70×10^{-8}
6	400.476	9.04×10^{-3}	5.64×10^{-8}
7	396.497	5.44×10^{-3}	3.46×10^{-8}
8	392.449	3.85×10^{-3}	2.50×10^{-8}
9	386.449	2.66×10^{-3}	1.78×10^{-8}
10	384.566	2.12×10^{-3}	1.44×10^{-8}
11	379.130	1.24×10^{-3}	8.64×10^{-9}
12	376.598	1.18×10^{-3}	8.31×10^{-9}
13	370.460	6.13×10^{-4}	4.46×10^{-9}
14	368.116	5.96×10^{-4}	4.40×10^{-9}
15	362.200	2.38×10^{-4}	1.81×10^{-9}
16	359.738	2.27×10^{-4}	1.75×10^{-9}
17	354.455	1.75×10^{-4}	1.39×10^{-9}
18	347.386	1.43×10^{-4}	1.18×10^{-9}
19	346.319	1.41×10^{-4}	1.08×10^{-9}

TABLE 5.4

Activation Energy Calculated From Arrhenius Plots

SLOWER PART

S/No.	DIODE No.	ACTIVATION ENERGY eV
1	E-112-III	1.032±0.012
2	E-112-II	1.027±0.022
3	AM-325-V	1.032±0.018

Fig. 5.13 ARRHENIUS PLOT

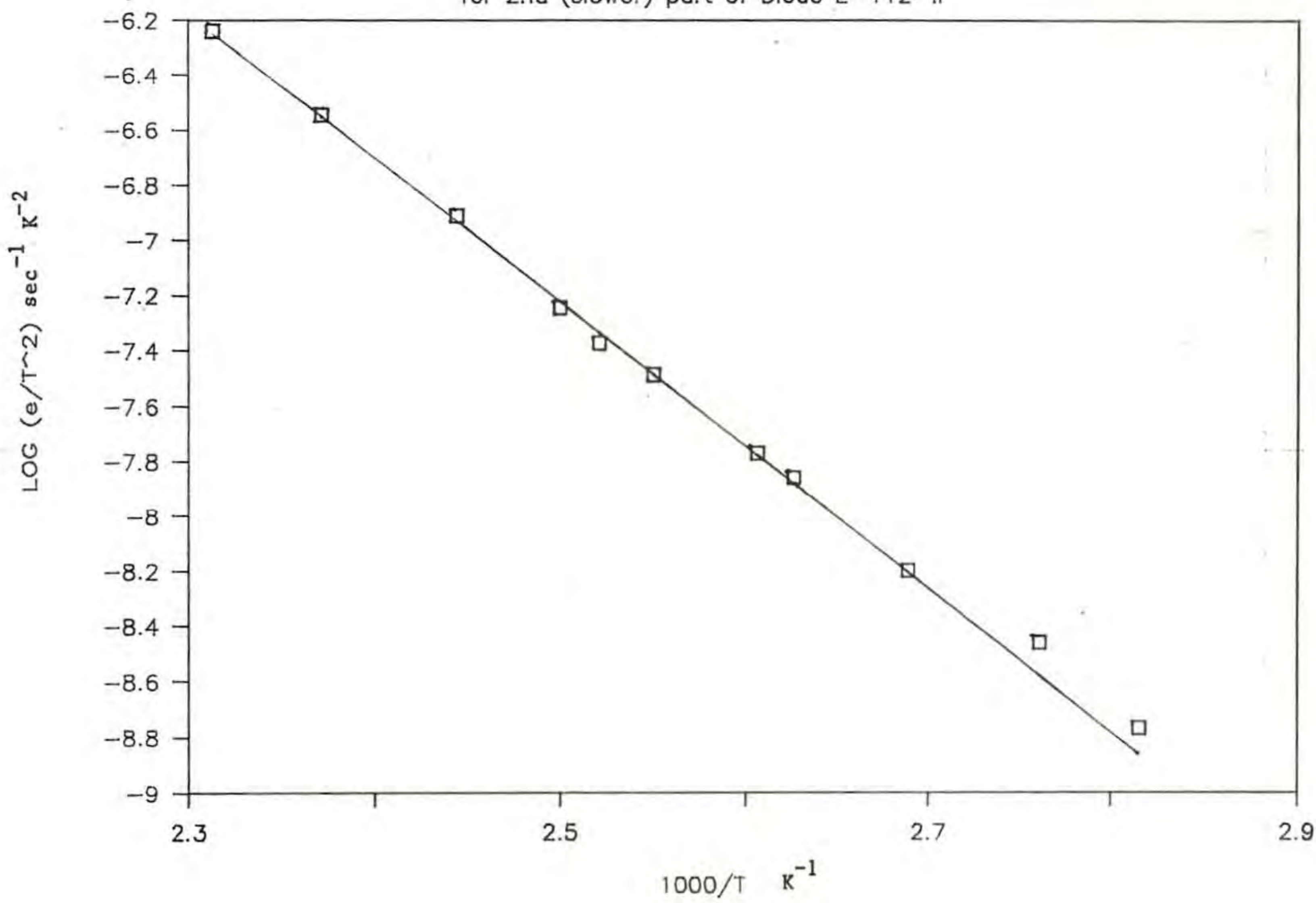


Fig. 5.14. *Arrhenius Plot*

for 2nd(slower) part of diode E-112-III

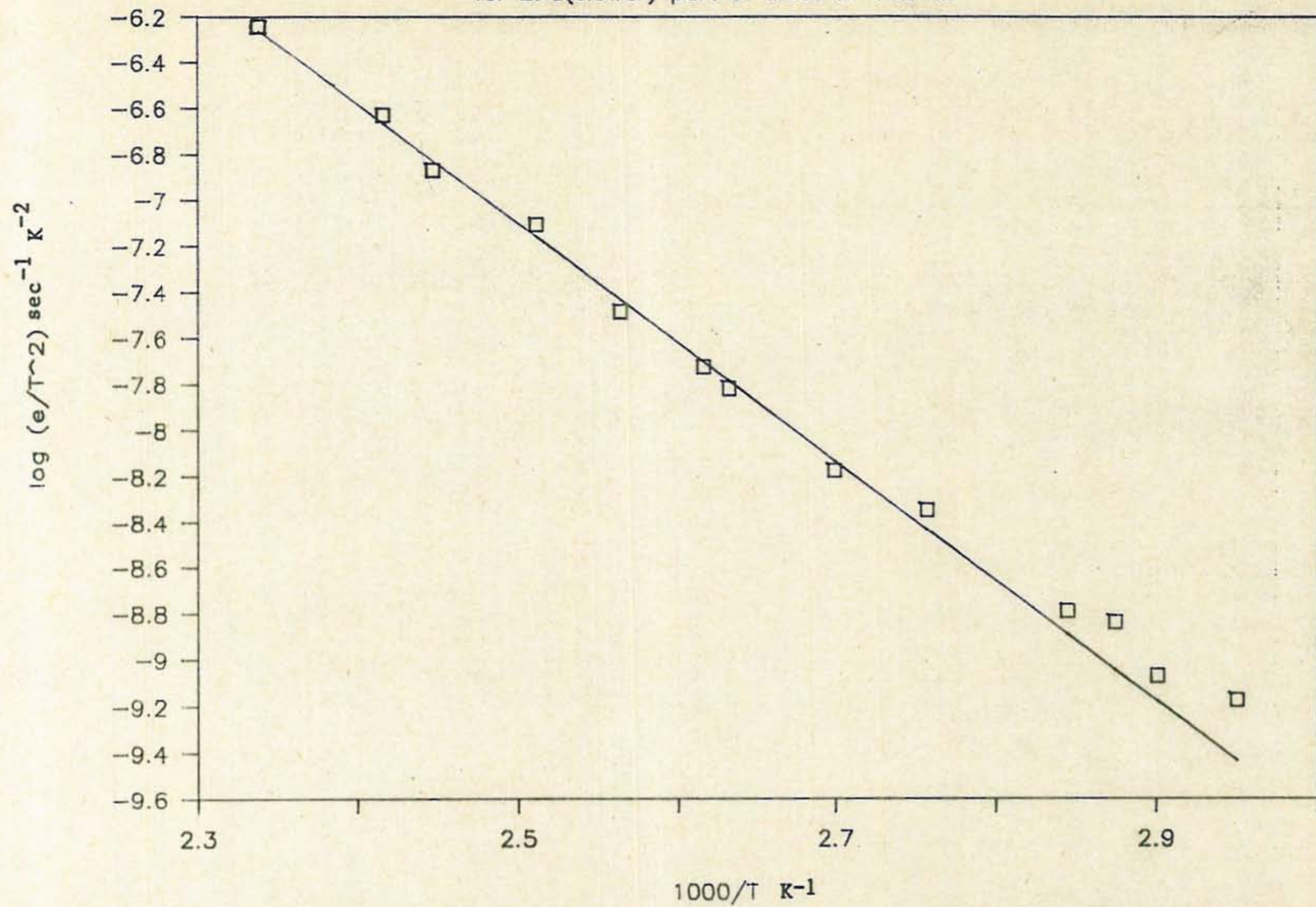
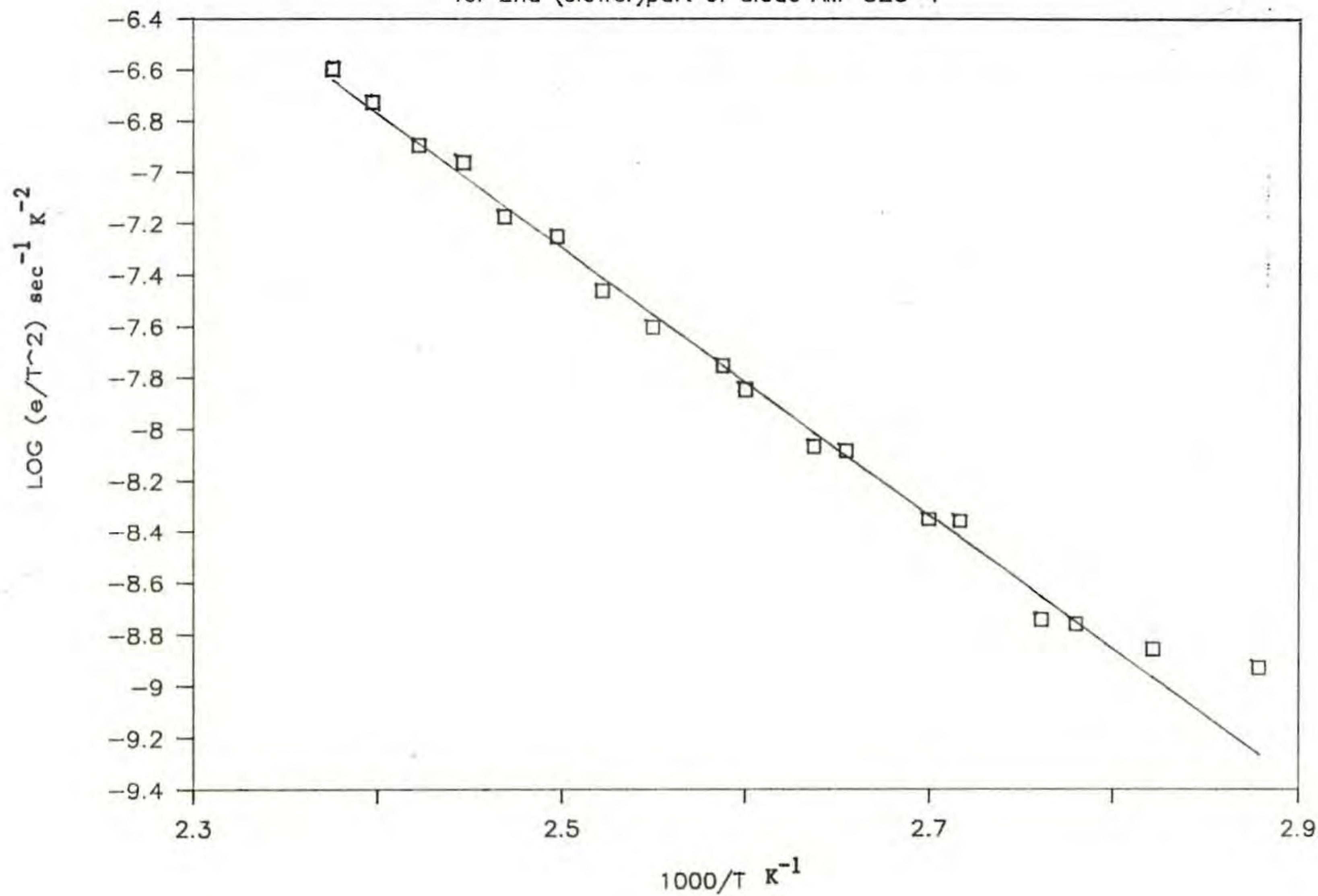


Fig. 5.15. *Arrhenius Plot*



emission rates. This corrected emission rate data for the three test diodes is given in tables 5.5, 5.6 and 5.7 and their Arrhenius plots are shown in Figs. 5.16, 5.17 and 5.18. The energies obtained from these Arrhenius plots are given in table 5.7.1 with an avarage value 0.94±0.02 eV.

5.3. DLTS MEASUREMENTS:

As earlier explained single shot measurements can go upto a particular temperature corresponding to a particular emission rate due to the limitations posed by the rise time of the x-t recorder. For higher emission rates DLTS measurements were carried out.

The experimental procedure for DLTS measurements was given in section 4.3.2. When reduced reverse-bias pulses were applied to diode No. E-112-II, a pronounced DLTS peak was observed. The temperature scans were taken for different emission rate window settings resulting in DLTS peaks, three of which are shown in Fig. 5.19. From these measurements, the resulting emission rate data is given in table 5.8. The Arrhenius plot of this data is shown in Fig. 5.20. which gives the activation energy $E_C - E_T = 1.02 \pm 0.02$ eV

5.4. COMBINATION OF DLTS AND SINGLE SHOT DATA:

For diode No. E-112-II, both single shot and DLTS data have been obtained. The emission rates obtained from DLTS measurements agree very closely with those of the second

TABLE 5.5

Emission Rate Data for (Corrected Part Transient) of

Diode # E-112-III

S/No.	TEMPERATURE K	EMISSION RATE (Corrected Part) sec^{-1}	$^{e}/T^{2}$ sec^{-1} K^{-2}
1	432.360	5.94×10^{-1}	3.18×10^{-6}
2	421.788	3.21×10^{-1}	1.81×10^{-6}
3	409.196	1.07×10^{-1}	6.39×10^{-7}
4	400.053	5.68×10^{-2}	3.55×10^{-7}
5.	396.592	4.51×10^{-2}	2.87×10^{-7}
6	392.112	3.40×10^{-2}	2.21×10^{-7}
7	383.645	1.64×10^{-2}	1.12×10^{-7}
8	380.717	1.46×10^{-2}	1.01×10^{-7}
9	371.902	6.45×10^{-3}	4.67×10^{-8}
10	362.177	3.50×10^{-3}	2.67×10^{-8}
11	355.231	2.03×10^{-3}	1.61×10^{-8}
12	384.578	1.62×10^{-3}	1.34×10^{-8}
13	346.058	1.10×10^{-3}	9.20×10^{-9}
14	338.990	4.16×10^{-4}	3.62×10^{-9}

TABLE 5.6

Emission Rate Data for (Corrected part Transient) of

Diode # E-112-II

S/No.	TEMPERATURE K	EMISSION RATE (Corrected Part) sec^{-1}	e_n/T^2 $sec^{-1}\ K^{-2}$
1	427.704	5.19×10^{-1}	2.84×10^{-6}
2	413.880	2.36×10^{-1}	1.38×10^{-6}
3	408.722	1.44×10^{-1}	8.62×10^{-7}
4	398.282	8.30×10^{-2}	5.23×10^{-7}
5.	390.128	2.95×10^{-2}	1.94×10^{-7}
6	382.360	1.79×10^{-2}	1.22×10^{-7}
7	380.025	2.21×10^{-2}	1.02×10^{-7}
8	370.510	5.88×10^{-3}	4.35×10^{-8}
9	362.717	3.56×10^{-3}	2.71×10^{-8}
10	351.500	1.45×10^{-3}	1.17×10^{-8}
11	347.885	8.77×10^{-4}	7.25×10^{-9}
12	344.750	5.58×10^{-4}	4.69×10^{-9}
13	338.920	3.07×10^{-4}	2.67×10^{-9}

TABLE 5.7

Emission Rate Data for (Corrected part Transient) of

Diode # AM-325-V

S/No.	TEMPERATURE K	EMISSION RATE (Corrected Part) sec^{-1}	e/T^2 $sec^{-1}\ K^{-2}$
1	421.098	3.12×10^{-1}	1.76×10^{-6}
2	417.217	2.62×10^{-1}	1.51×10^{-6}
3	412.878	1.80×10^{-1}	1.06×10^{-6}
4	408.805	1.37×10^{-1}	8.23×10^{-7}
5.	405.103	9.63×10^{-2}	5.87×10^{-7}
6	400.476	8.23×10^{-2}	5.13×10^{-7}
7	396.497	4.43×10^{-2}	2.82×10^{-7}
8	392.449	4.25×10^{-2}	2.76×10^{-7}
9	386.449	2.94×10^{-2}	1.97×10^{-7}
10	384.566	2.05×10^{-2}	1.39×10^{-7}
11	379.130	1.43×10^{-2}	9.96×10^{-8}
12	376.598	1.17×10^{-2}	8.26×10^{-8}
13	370.460	7.43×10^{-3}	5.42×10^{-8}
14	368.116	6.98×10^{-3}	5.15×10^{-8}
15	362.200	3.65×10^{-3}	2.78×10^{-8}
16	359.738	3.10×10^{-3}	2.40×10^{-8}
17	354.455	1.87×10^{-3}	1.49×10^{-8}
18	347.386	1.66×10^{-3}	1.37×10^{-8}
19	346.319	2.28×10^{-3}	1.90×10^{-8}

TABLE 5.8

Emission Rate Data (DLTS Measurements) for

Diode # E-112-III

S/No.	TEMPERATURE K	EMISSION RATE sec^{-1}	e/T^2 $Sec^{-1}K^{-2}$
1	474.640	2.26	1.00×10^{-5}
2	467.130	1.58	7.26×10^{-6}
3	462.395	1.08	5.07×10^{-6}
4	453.690	7.23×10^{-1}	3.51×10^{-6}
5.	446.850	4.52×10^{-1}	2.26×10^{-6}
6	442.531	3.39×10^{-1}	1.73×10^{-6}
7	436.980	2.26×10^{-1}	1.18×10^{-6}
8	428.995	1.36×10^{-1}	7.37×10^{-7}
9	424.970	1.05×10^{-1}	5.83×10^{-7}

TABLE 5.7.1

Activation Energy Calculated From Arrhenius Plots

FASTER PART

S/No.	DIODE No.	ACTIVATION ENERGY eV
1	E-112-III	0.915±0.021
2	E-112-II	0.959±0.019
3	AM-325-V	0.918±0.021

Fig. 5.16. Arrhenius plot
for corrected data of diode E-112-II

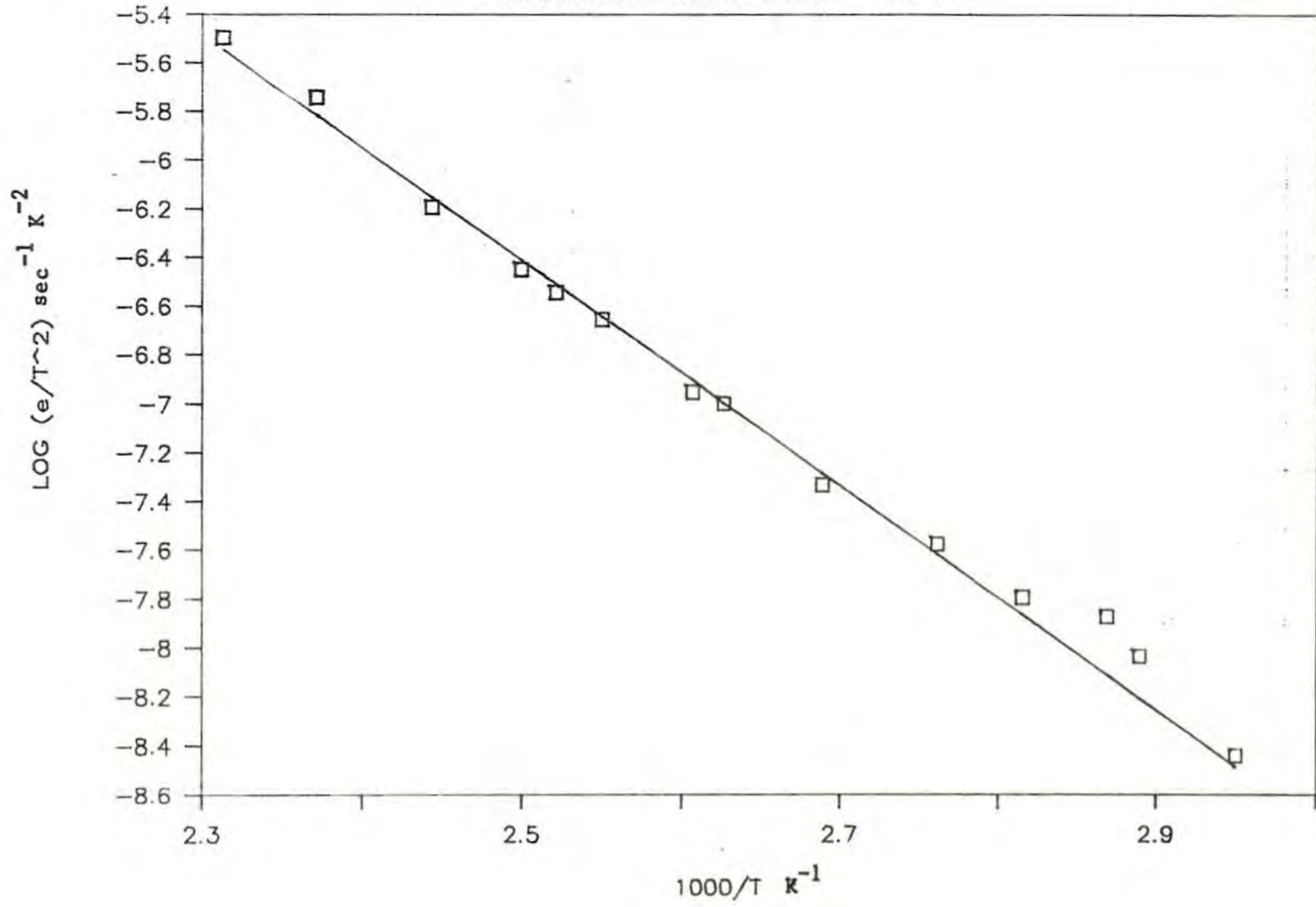


Fig. 5.17. Arrhenius plot

for corrected data of diode E-112-III

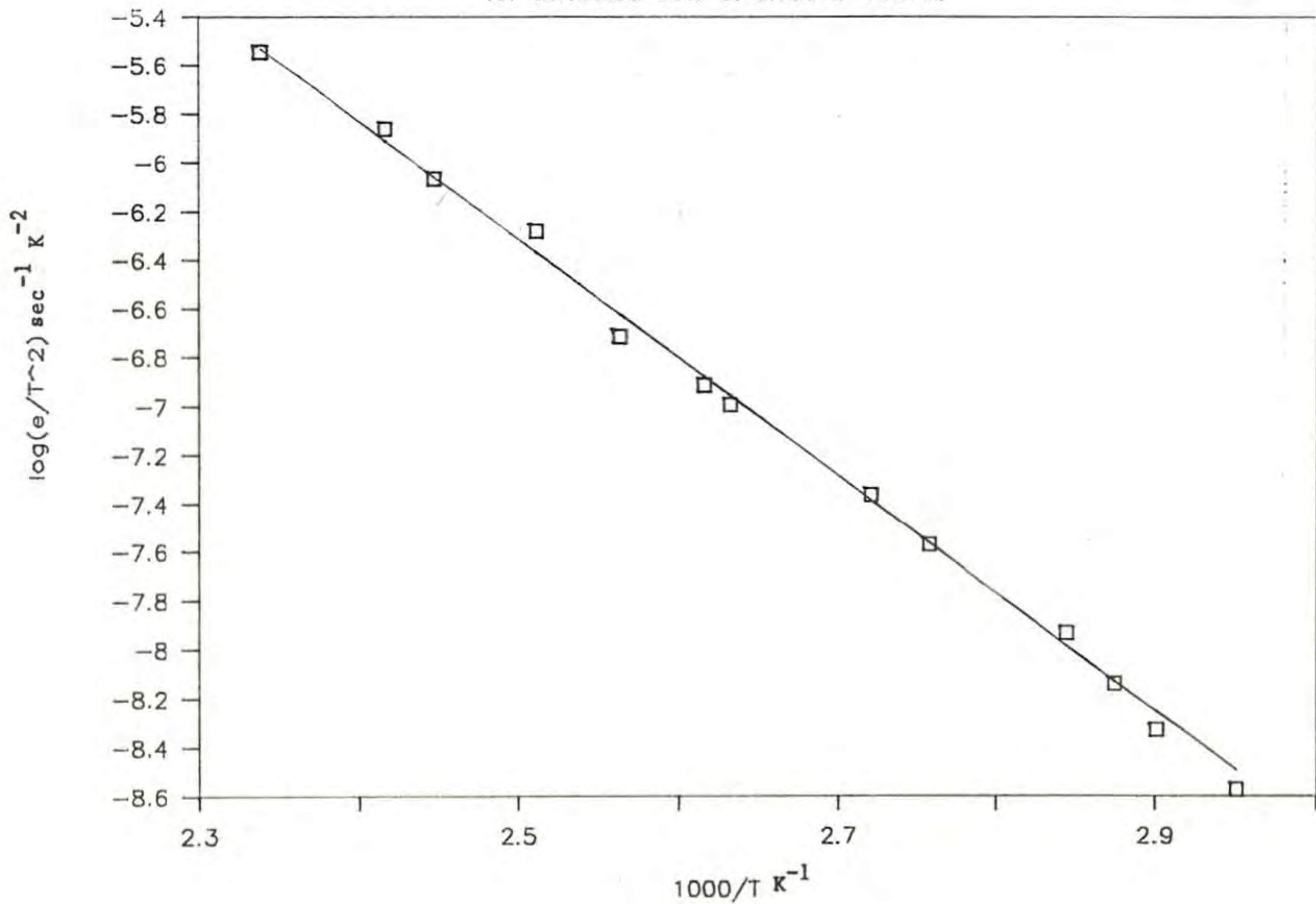
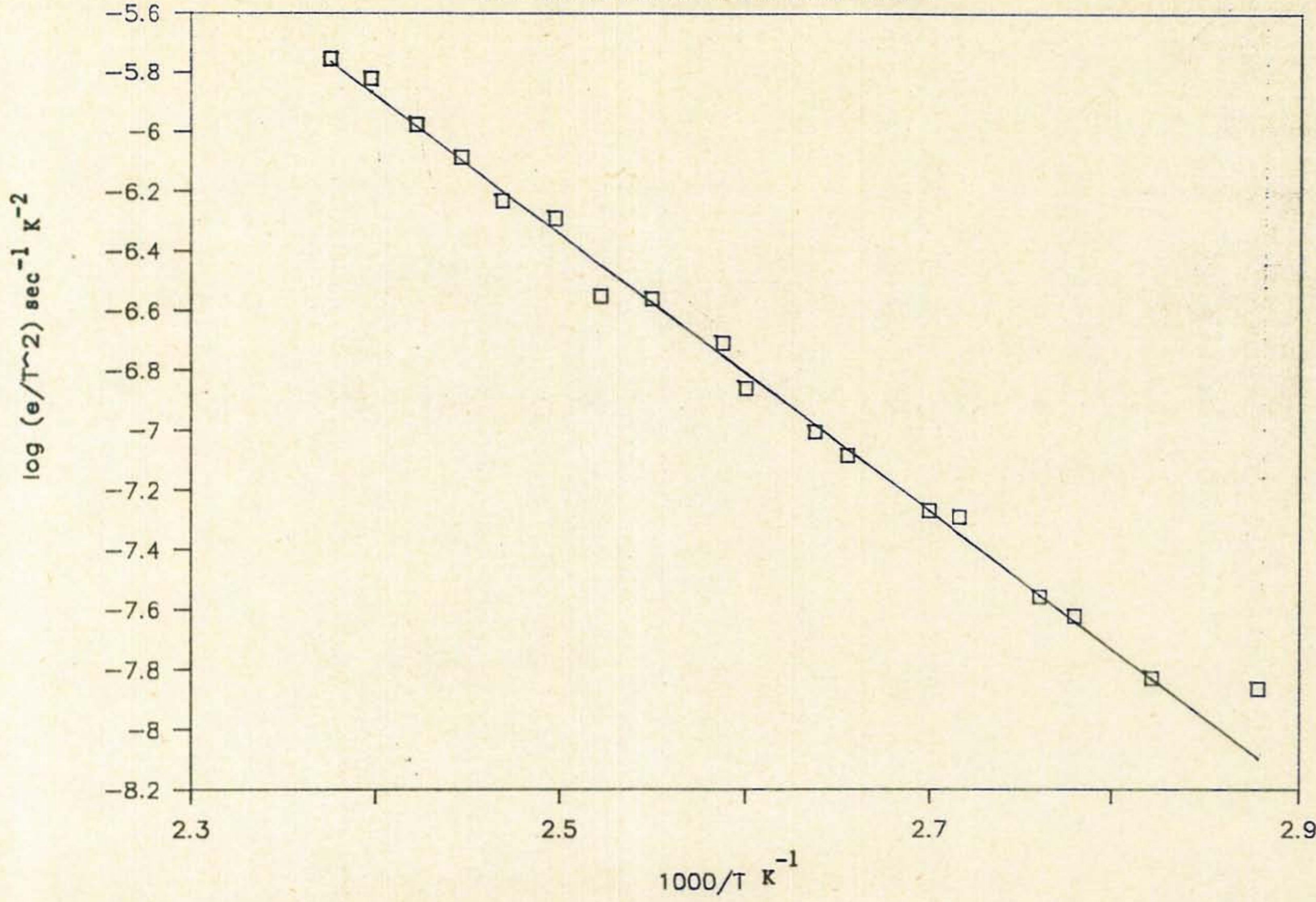


Fig. 5.18. Arrhenius plot
for corrected data of diode AM–325–V



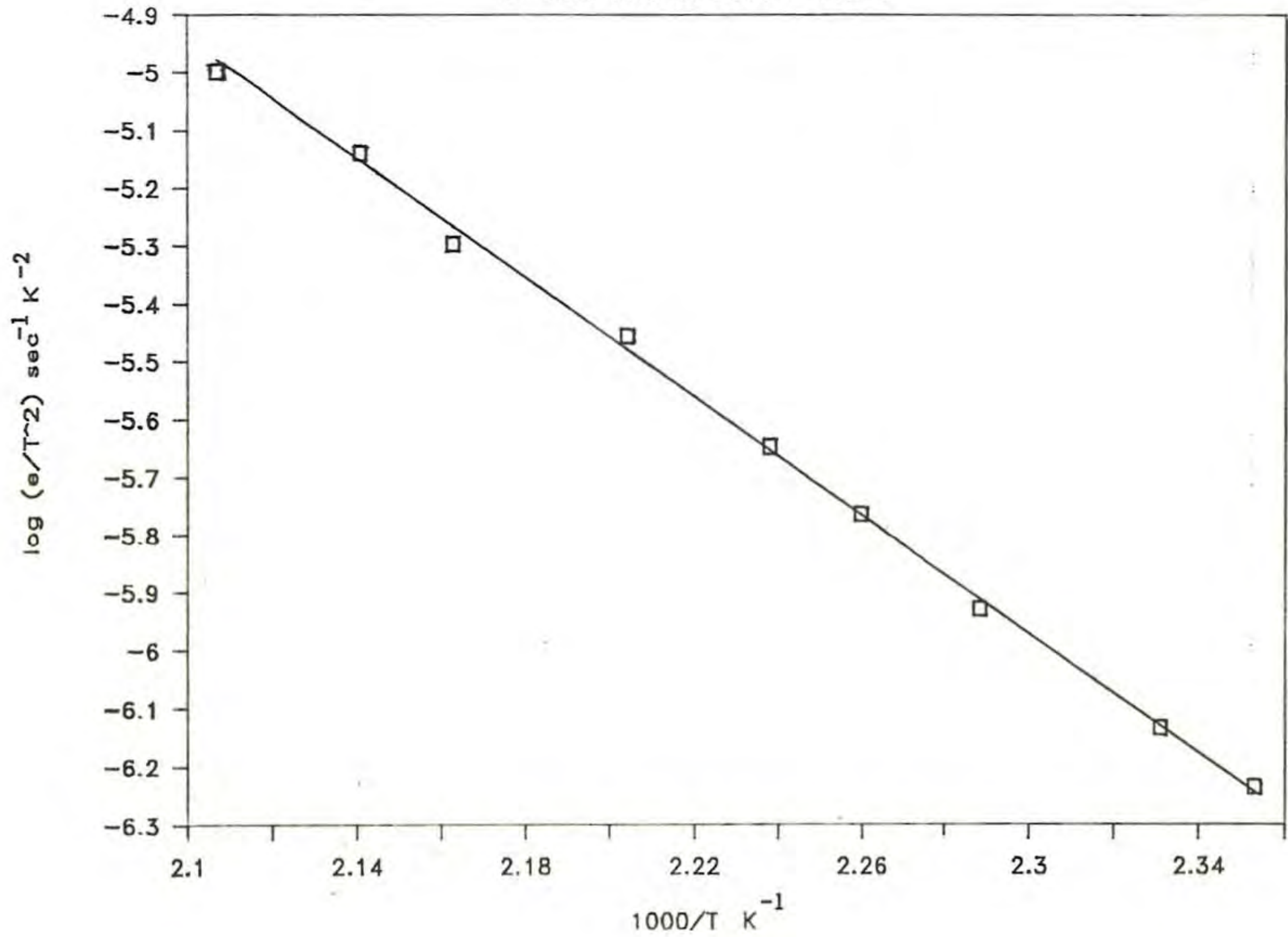


Fig.5.20. Arrhenius Plot

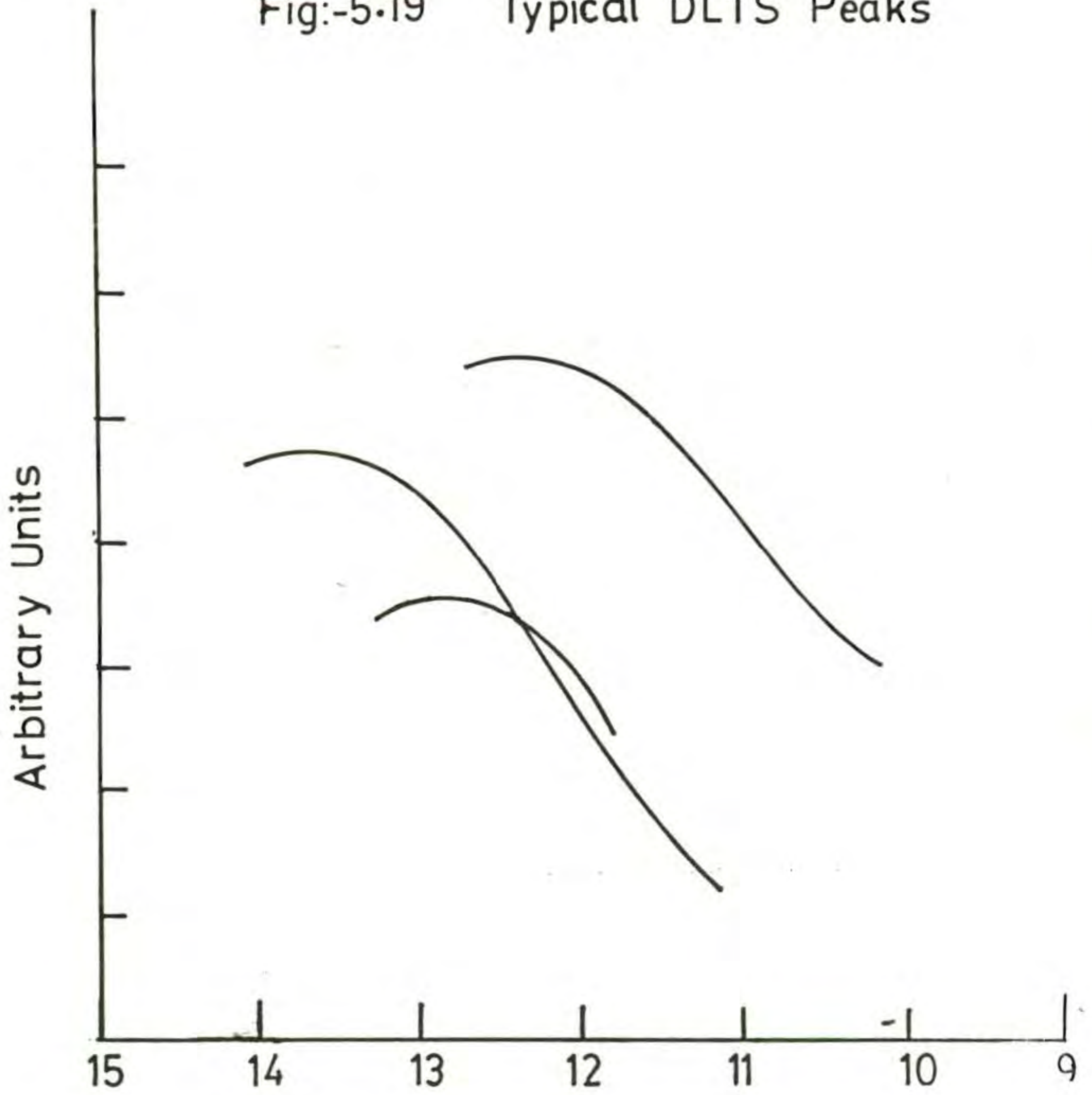


Fig:-5·19 Typical DLTS Peaks

(long-time) part of the single shot transients. This means that the DLTS peak was caused by the same level that gave the second part of the single shot transients. The two sets of data were ploted in Fig.5.14 and Fig.5.20 respectively. The two data together are given in table 5.9 and the Arrhenius plot is shown in Fig. 5.21. In this way we get emission rate data over four decades. The activation energy obtained from this combined Arrhenius is 1.05 ± 0.02 eV.

5.5. CONCENTRATION :

After calculating the energy of the deep level its concentration was calculated. The values given here are calculated by using the relation 3.27. This concentration was calculated for each temperature and then averaged for each diode.

Data for 1.03 eV Level

S.No.	Diode No.	Concentration
1.	E-112-III	2.00×10^{14} cm^{-3}
2.	E-112-II	8.87×10^{14} cm^{-3}
3.	AM-325-V	7.98×10^{14} cm^{-3}

Data for 0.94 eV Level

S.No.	Diode No.	Concentration
1.	E-112-III	1.06×10^{14} cm^{-3}
2.	E-112-II	5.99×10^{14} cm^{-3}
3.	AM-325-V	1.17×10^{15} cm^{-3}

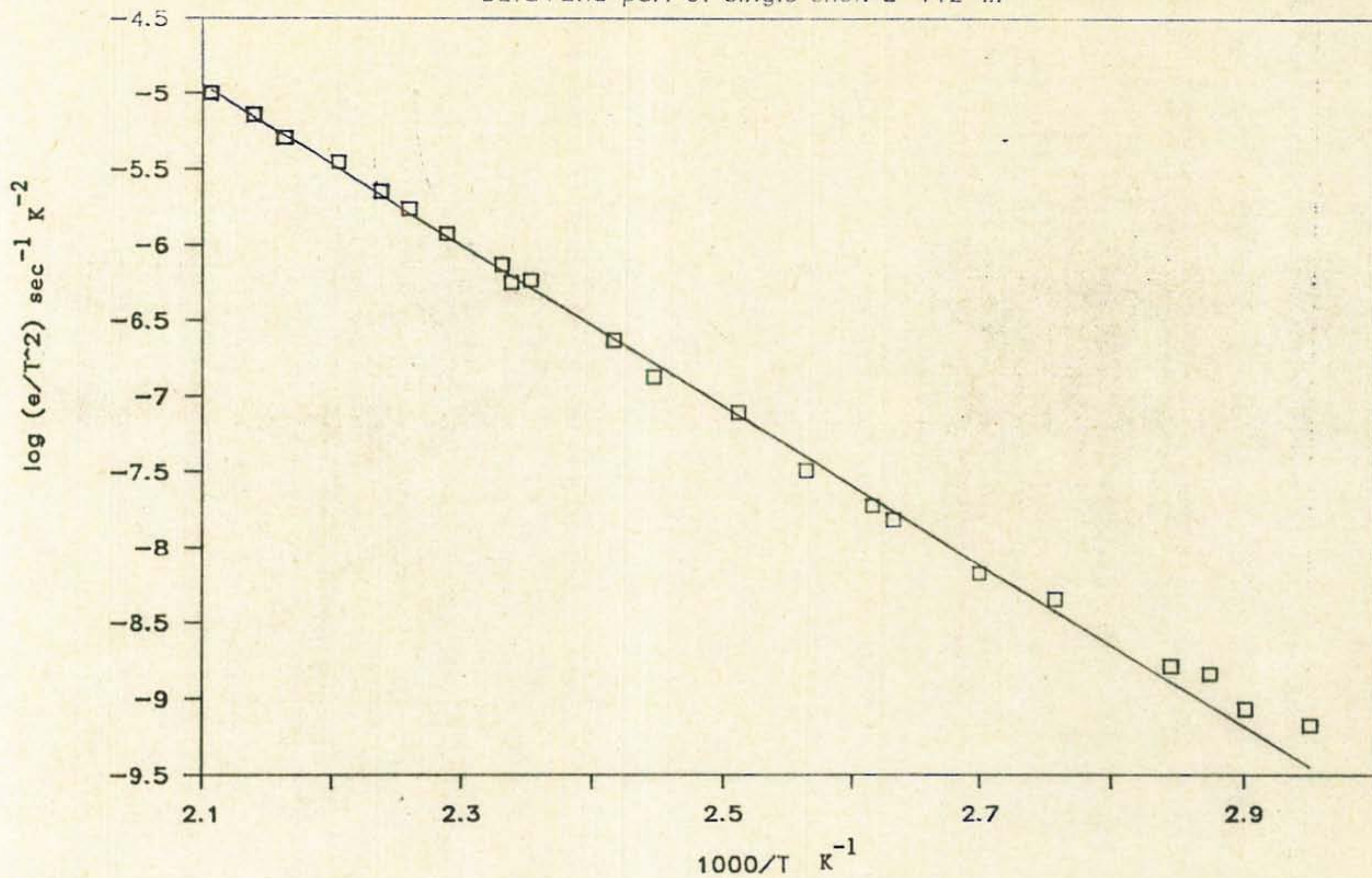
TABLE 5.9

Emission Rate Data (DLTS+SINGLE SHOT Measurements) for

Diode # E-112-III

S/No.	TEMPERATURE K	EMISSION RATE sec^{-1}	e/T^2 sec^{-1} K^{-2}
1	474.640	2.26	1.00×10^{-5}
2	467.130	1.58	7.26×10^{-6}
3	462.395	1.08	5.07×10^{-6}
4	453.690	7.23×10^{-1}	3.51×10^{-6}
5.	446.850	4.52×10^{-1}	2.26×10^{-6}
6	442.531	3.39×10^{-1}	1.73×10^{-6}
7	436.980	2.26×10^{-1}	1.18×10^{-6}
8	428.995	1.36×10^{-1}	7.37×10^{-7}
9	427.704	1.03×10^{-1}	5.66×10^{-7}
10	424.970	1.05×10^{-1}	5.83×10^{-7}
11	413.880	4.03×10^{-2}	2.35×10^{-7}
12	408.722	2.25×10^{-2}	1.35×10^{-7}
13	398.282	1.24×10^{-2}	7.85×10^{-8}
14	390.128	5.00×10^{-3}	3.29×10^{-8}
15	382.360	2.77×10^{-3}	1.89×10^{-8}
16	380.025	2.21×10^{-3}	1.53×10^{-8}
17	370.510	9.22×10^{-4}	6.72×10^{-9}
18	362.717	5.94×10^{-4}	4.51×10^{-9}
19	351.500	2.02×10^{-4}	1.63×10^{-9}
20	347.885	1.77×10^{-4}	1.46×10^{-9}
21	344.750	1.02×10^{-4}	8.58×10^{-10}
22	338.920	7.70×10^{-5}	6.70×10^{-10}

Fig.5.21. Arrhenius Plot.



5.6. FIELD EFFEC :

It was observed that a change in applied reverse bias changed the total magnitude of the transients which is obvious since on applying the reverse bias, depletion region width would increase and more deep levels will empty and consequently the capacitance will increase. It was also abserved that an increase in applied reverse bias increased the emission rates. Three measurements were taken on different applied reverse biases. The observed data is given in the table below.

S.No.	Applied Reverse Bias	e_1 (corrected) $(sec.)^{-1}$	e_2 $(Sec.)^{-1}$	ΔC_∞ (pF)
1.	-2V	3.28×10^{-2}	6.28×10^{-3}	0.06
2.	-5V	5.24×10^{-2}	6.85×10^{-3}	0.94
3.	-7V	6.67×10^{-2}	9.76×10^{-3}	0.97

These measurements were taken on the diode E-112-III.

5.7. DISCUSSION :

To sum up the above results, two deep levels are seen in single shot measurements with activation energies 0.94 eV and 1.03 eV. Itshould be noted here that the Arrhenius plot of the 0.94 eV level shows considerable scatter and it is not observed in DLTS measurements. Clearly more work is needed on this level before its origin is commented upon. Such

work is underway in this laboratory presently.

The DLTS measurements reveal only one level which seems to be the same as the level measured on single shots. This level has activation energy similar to the one seen in TSCAP measurements earlier[2]. Thus this is now a well established level in green GaP LEDs and it is interesting to comment upon its origin.

This deep level seems to be one of the deepest native defects ever observed in LPE GaP. The comparason of the activation energy with published results indicates the following possible candidates for it:

Oxygen[3]	state 1	1.18 eV
	state 2	1.08 eV
Deep level induced by current stressing(thought to be P_{Ga})[4]		1.18 ± 0.05eV
P_{Ga} antisite[5] (from photo-EPR)		1.10 ± 0.10eV
D5[6]		1.03 eV
D6[6]		1.06 eV

The samples under consideration contain no intentional oxygen - any inadvertent oxygen would not be expected to be present in such concentrations as observed in the present experimental work. The identification of this mid-gap centre with oxygen is therefore ruled out. The deep donor D5 and D6 observed in MOVPE (metal-organic vapour phase epitaxy) GaP[6] have very different emission rates as compared to the the investigated level. From the above list, therefore P_{Ga}

antisite defect appears to be the only likely candidate for our mid-gap level. The emission rates measured by Ferenczi etal[4] for the deep level attributed to P_{Ga} in their forward current stressing experiments are somewhat smaller than the present measured values. However, in view of their admittedly poor data over very limited temperature range, it is possible that this discrepancy between our data is insignificant. This identification with P_{Ga} defect is, however, lacking any direct proof. Another interesting speculation could be that our mid-gap level may be the analog of the well known EL2(in GaAs) centre in GaP. Clearly further work will be needed to establish the identity of the mid-gap centres detected by us definitively.

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