DEEP LEVEL TRANSIENT SPECTROSCOPY ON SEMICONDUCTOR MATERIALS

FINAL TECHNICAL REPORT

PAKISTAN SCIENCE FOUNDATION
PROJECT NO. PSF-C-QU/PHYS.(44)

SEMICONDUCTOR PHYSICS LABORATORY
DEPARTMENT OF PHYSICS
QUAID-I-AZAM UNIVERSITY
ISLAMABAD
1989

FINAL TECHNICAL REPORT

Project Title: Deep Level Transient Spectroscopy on Semiconductor Materials.

Principal Investigator Dr.M. Zafar Iqbal

Institution: Department of Physics,Quaid-i-Azam University, Islamabad.

Project Number PSF-C-QU/Phys(44).

Signature and Stamp of Principal Investigator

M Zafar Iqbal

DR. M. ZAFAR IQBAL
Principal Investigator
Project C-QU/Phys (44)
Quaid - i - Azam University
ISLAMABAD

Signature and Stamp of the Vice-Chancellor

Vice-Chancellor,
Quaid-I-Azam University
ISLAMABAD

Dated

SUMMARY

Deep Levels in Crystalline Semiconductors, caused by impurities and defects, are an important field of research both from pure physics as well as applications point of view. This project concerned itself with the study of deep levels by establishing the standard technique of Deep Level Transient Spectroscopy (DLTS) for the first time in Pakistan. The major part of the project consisted of the study of the deep level content of green and red light emitting diodes (LEDs) prepared from Gallium Phosphide (GaP). The deep levels present in this material were mostly inadvertant. Another part of the project concerned itself with the study of deep levels resulting from deliberate doping of Silicon with known impurities.

The DLTS set-up has been successfully installed and expertise for the technique fully developed so that now deep level spectroscopy can be performed on any Semiconductor junction for a complete characterization of its deep level content.

The study of green LEDs has shown the presence of five electron-emitting and three hole-emitting levels. Emission rate data for these levels have been obtained. Three of these levels have been the focus of attention. It was found that thermal emission rates of the already known 0.85 eV hole level were weakly field dependent. This field dependance was investigatged in detail. By comparing with the previously published data on it and by fitting our results with theoretical models, important conclusion as to the origin and microscopic structure of this level were drawn.

In the case of another well known level, the nitrogen related 0.45 eV level, it was discovered that its electron capture cross-sections were strongly temperature dependent. This temperature dependance was investigated in detail. The results seem to pose a question to the established model of temperature dependance of capture cross-sections.

The dominant deep levels in the green LEDs are two mid-gap levels that have not been reported in literature previously. Detailed charactrization of these levels was accomplished.

Investigating the red emitting LEDs it was discovered that the important oxygen level in GaP has strongly ~~temperature~~ field dependent thermal emission rates. This field effect was studied in detail and the results are expected to modify the well-estbalished models for this level.

DETAILED REPORT

I. INTRODUCTION:

The significance of deep electronic levels lying in the band-gap of semiconductors is well-established. The study of these levels on the one hand helps improving the efficiency of electronic devices and on the other hand gives important insight into the physics of semiconductors. The purposes of this project included both these aspects making it important from applied as well as pure physics point of view. The specific purposes of this project can be divided into 3 categories :

(a) ESTABLISHMENT OF DLTS FACILITY IN PAKISTAN:

Deep Level Transient Spectroscopy (DLTS) has become a standard technique for the investigation of impurity (defect) centres in semiconductors. In semiconductor research work all over the world, DLTS set up is considered to be an essential facility both in industrial and academic laboratories. Prior to this project no DLTS facility existed in Pakistan. One purpose of this project was, therefore, to establish DLTS instrumentation and expertise.

(b) DEEP LEVEL CHARACTERIZATION OF GaP LIGHT EMITTING DIODES (LED's)

The GaP red and green light-emitting diodes (LED's) are known for their low quantum efficiency. Deep-levels acting as non-radiative recombination centres are the main source of this low efficiency. Thus work on the deep level content of these LED's is of technological significance. One main purpose of the project was to characterize the deep levels in these LED's in general and then concentrate on the finer details of some of the prominent levels. Detailed investigations of properties like field dependence of thermal emission rates and temperature dependance of capture cross-sections was expected to shed light on the microscopic nature of the defects associated with the particular deep levels investigated.

(c) DELIBERATELY INTRODUCED DEEP IMPURITIES IN SILICON.

Silicon, the most widely used semiconductor material in electronics industry, is also the one that is most extensively studied. To understand the behaviour of deep levels and their effects on device properties, known impurities are deliberately added into silicon and their characteristics are studied. One aim of this project was to pursue this line. The plan included diffusion of impurities in this lab for which equipment was to be obtained from sources other than PSF.

(b.1.ii) THE FIELD EFFECT ON THE LEVEL H_3(0.85 eV)

Detailed investigations on the H_3 level were carried out. it was found that the DLTS peak, for a fixed rate window (emission rate) shifted in temperature when the standing reverse bias was changed. This showed that the rate of hole emission from this level increased with the electric field present in the space-charge region. The detailed field dependance of the hole emission rates was measured using DLTS. The results have already been published in the Journal of Applied Physics, Vol. 62, pp. 4471 (1987), which is attached as Appendix I.

(b.1.iii) CAPTURE CROSS-SECTIONS OF THE LEVEL E_3(0.45 eV).

E_3 was identified as the well known Nitrogen related level which is always found in Nitrogen-doped GaP. It was discovered that the electron capture cross-sections (σ_n) of this level were strongly temperature dependant. A detailed study revealed that σ_n for E_3 decreases exponentially with the inverse of temperature. Detailed measurements on the temperature dependence of σ_n for this level have been carried out. The results have been reported in the 19th International Conference on the Physics of Semiconductors held at Warsaw in August 1988. The paper has been accepted to be published in the conference proceedings. A copy of the paper is attached in Appendix II.

(b.1.iv) CHARACTERIZATION OF THE MID-GAP LEVEL E_5 :

E_5 is the dominating electron level in our green emitting LEDs. Detailed measurements of the rates of electron emission from and capture into it have been carried out. The results have been the subject of two research papers. One was presented at the Regional Conference on Semiconductors and Physics of Materials, Kuala Lumpur, Malaysia, June 15-19, 1987 and the other is being submitted for publication in the Journal of Applied Physics. Copies of both are attached as Appendices III and IV.

(b.1.v) PECULIAR NATURE OF THE LEVEL H_2 :

It has been found that the level H_2 has very interesting properties. it seems that its concentration increases dramatically at the application of forward bias at high temperature but goes back to almost undetectable value within a few hours. The details of this aspect of H_2 still need to be worked out.

measurements on the Si:Pt mid-gap level. These measurements were carried out using DLTS. In this measurement the height of the DLTS peak S is measured as a function of the excitation pulse width t_p. If S_o is the saturation peak height, then $\log(S_o-S)$ vs t_p is supposed to give a straight line, the slope of which provides the capture rate. Fig.4 shows such a plot obtained by us. As seen in the figure the plot is not a straight line. This is probably due to the capture in the edge-of-the-space-charge region which is expected to give rise to such behaviour particularly for levels lying away from the edges of the band gap. This level being mid-gap is very likely to exhibit such behaviour. The upper-limit on the capture cross-sections, however, can be specified from the initial (short-time) slope of the curve in Fig.4. This gives the electron capture cross-section to be 1×10^{-16} cm^2. Further work to improve this data and measure the cross-sections at different temperatures is projected for future.

The silver doped silicon samples show two levels at E_c-0.54 eV and E_v+0.34 eV. The work on silver is in progress.

III DISCUSSION:

Because of the low quantum efficiency of Light emitting diodes (LEDs) produced using GaP, the deep level content of such LEDs has been the focus of attention of many researchers working in this field for the last two decades. We have, for the first time, carried out such detailed measurements as field effect on thermal emission rates and temperature dependence of capture cross-sections etc. on the important deep levels in GaP. The discovery and detailed characterisation of the dominant mid-gap level in green LEDs, is also very significant. The field effect on the thermal emission rates of the oxygen level is another important work since oxygen in GaP has been a subject of detailed studies and controversies in the past but the field effect has been described for the first time. This could lead to re-evaluation of the existing models about this important level.

The work on the mid-gap level in platinum diffused silicon is also very significant, since it gives the answer to the puzzle of large recombination rates in platinum doped silicon which could not be explained satisfactorily on the basis of the two established levels related to platinum in silicon.

The investigations carried out on light emitting diodes and Si:Pt are both very significant from technological point of view and shall be useful in industrial applications of LED's and fast switching devices.

IV CONCLUSIONS:

The important conclusions, of the work done under this project can be summarized briefly as follows:

(i) The thermal emission from the 0.85 eV hole level in GaP is weakly field dependent and can be explained by Poole-Frenkel Effect.

(ii) The 0.85 eV level in GaP reported in many research papers is probably not a single level. Various researchers seem to be observing thermal emission from more than one levels of similar energy but different origins.

(iii) The capture cross-section of the 0.45 eV electron level, always present in N-doped GaP is strongly temperature dependent, decreasing exponentially with inverse of temperature.

(iv) The 0.45 eV level in GaP has "true" depth of ~ 0.23 ±0.02 eV below conduction band.

(v) The extrapolated electron capture-cross-section of the 0.45 eV level in GaP is ~ 10^{-12} cm^2 which is one of the highest ever reported values for any deep level in a semiconductor.

(vi) Two inadvertent near mid-gap electron-emitting levels are the dominant deep levels in green LED's of GaP prepared by liquid phase epitaxy (LPE).

(vii) One of the mid-gap levels in LPE GaP is a good candidate for the counterpart, in GaP, of the well-known EL-2 level found in GaAs.

(viii) Thermal emission of electrons from the oxygen level in GaP is strongly field dependent, the emission rate varying almost exponentially with field in the space-charge region.

(ix) The platinum related mid-gap level is the dominating recombination centre in platinum doped silicon.

V NEED FOR ADDITIONAL RESEARCH:

(a) As mentioned in sub-section b.1.5 of section (ii) the peculiar nature of the level H_2 needs further work.

(b) The field effect data on the oxygen level in GaP, as reported in appendix V requires detailed theoretical interpretation. This work is currently in progress.

(c) The Zn-O complex in GaP has been reported to exhibit field dependent thermal emission. However, the detailed measurements on this do not exist. This work could be undertaken at this stage.

(d) The temperature dependence of the capture cross-sections of the mid-gap levels is difficult to perform using DLTS as explained in the appendix IV. However, other methods like single shot technique, coupled with pulsed excitation or pulse train method could be tried for this purpose.

VI PROBLEMS FACED AND NEED FOR EXTENSION OF THE PROJECT:

A very important part of the present project was to carry out deep level investigations on the indigenously prepared samples. However, this part depended firstly upon the import of semiconducting materials and secondly upon acquiring the major equipment from sources other than PSF. For the import of semiconductor materials, which were to be used as base materials, our project contained a provision of Rs.30,000. However, for this sum only small quantities of materials could be imported and the foreign suppliers are reluctant to sell such small quantities. We had a prolonged correspondence with them and by the time we succeeded in convincing them to supply us the materials, the project was nearing its end and the PSF refused to release the funds.

As for the major equipment, namely a diffusion furnace, we were able to acquire one through our international collaborative arrangements in the beginning of 1987. However, it took months to get it cleared from the customs and then many more months to get a transformer installed by WAPDA for its high power requirements. Now the furnace is working but the project duration is over. We are, therefore, depending upon the extension of the project, including the release of the Rs.30,000 for the semiconductor materials, to complete this part of the project.

VII LIST OF PUBLICATIONS:

1. Field effect on the thermal emission from the 0.85 eV hole level in GaP, by N. Baber and M. Zafar Iqbal, in Journal of Applied Physics Vol. 62, p.4471 (1987).

2. Transient capacitance measurements on a mid-gap level in GaP, by A. Ali, N. Zafar and M. Zafar Iqbal, in Proceedings of the regional conference on Semiconductors and Physics of Materials, Kuala Lumpur, Malaysia, June 15-19, 1987.

3. Capture cross-sections of the 0.45 eV level in GaP, N. Baber and M. Zafar Iqbal, accepted for publication in the Proceedings of the 19th International Conference on the Physics of Semiconductors (ICPS), Warsaw, Poland, 15-19 August 1988.

4. Field dependence of thermal emission from oxygen in GaP by Umar S. Qureshi, M. Zafar Iqbal and N. Baber, accepted or publication in the proceedings of the 15th International onference on Defects in Semiconductors, Budapest, Hungary, August 22-26, 1988.

5. Electrical characterization of inadvertent mid-gap levels in GaP, by M. Zafar Iqal, Asghar A. Gill, and N. Baber, submitted for publication to the Journal of Applied Physics.

6. Role of the mid-gap level as the dominant recombination centre in Platinum doped Silicon, to be submitted to Applied Physics Letters.

VIII GRADUATE STUDENTS:

The folloeing post-graduate students, who assisted in the conduct of research, recieved their M.Phil. degrees during the life of the grant.

1. Asghar Ali Gill
2. Muhammad Saeed
3. Muhammad Asghar

Mr. Asghar Ali Gill subsequently registered and started work towards his Ph.D. Another M.Phil student, Umar Saeed Qurashi also assisted in the conduct of research and is about to submit his dissertation for M.Phil.

IX LIST OF SCIENTISTS:

The following scientists actively participated in the research pertaining to the project:

1. Dr. M. Zafar Iqbal
2. Dr. Nasim Baber
3. Dr. Nasim Zafar.

TABLE I

Levels observed in green-emitting GaP LEDs

Name of Level	Thermal Activation Energy E_T
Electron levels	
E1	0.21 eV
E2	0.26 eV
E3	0.42 eV
E4	0.88 eV
E5	1.00 eV
Hole levels	
H1	between 0.2 and 0.4 eV
H2	0.64 eV
H3	0.81 eV

FIGURE CAPTIONS:

Fig.1: The DLTS scan of a p^+n junction green-emitting diode.

Fig.2: I/C^2 vs V_R plot of a green-emitting diode giving the built-in voltage $V_B = 1.9$ V.

Fig.3: I/C^3 vs V_R plot of a red-emitting diode giving the built-in voltage $V_B = 2$ V.

Fig.4: Variation of DLTS peak height S from its saturation value S_o as the pulse width t_p is varied, for the mid-gap platinum level in silicon.

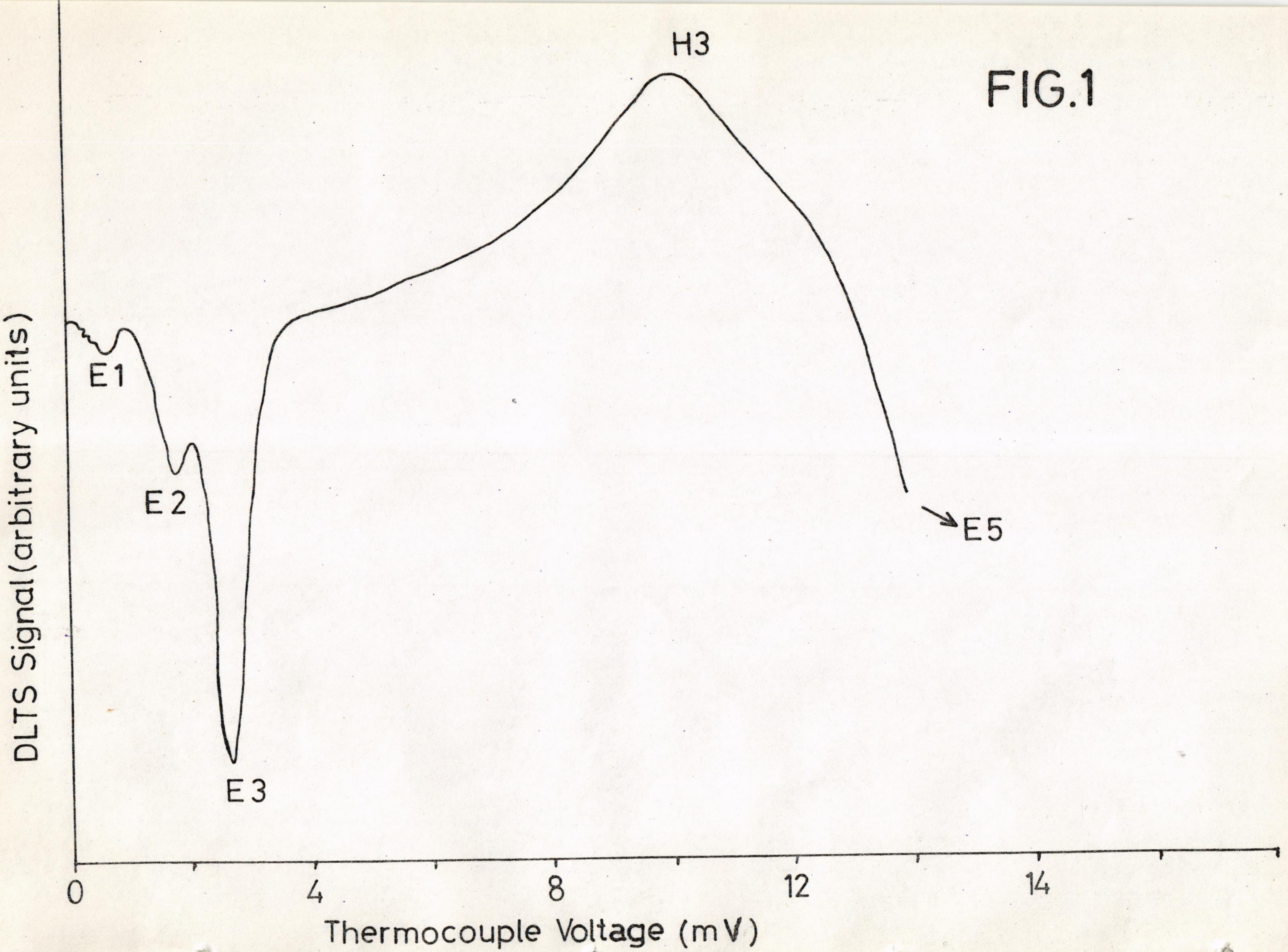
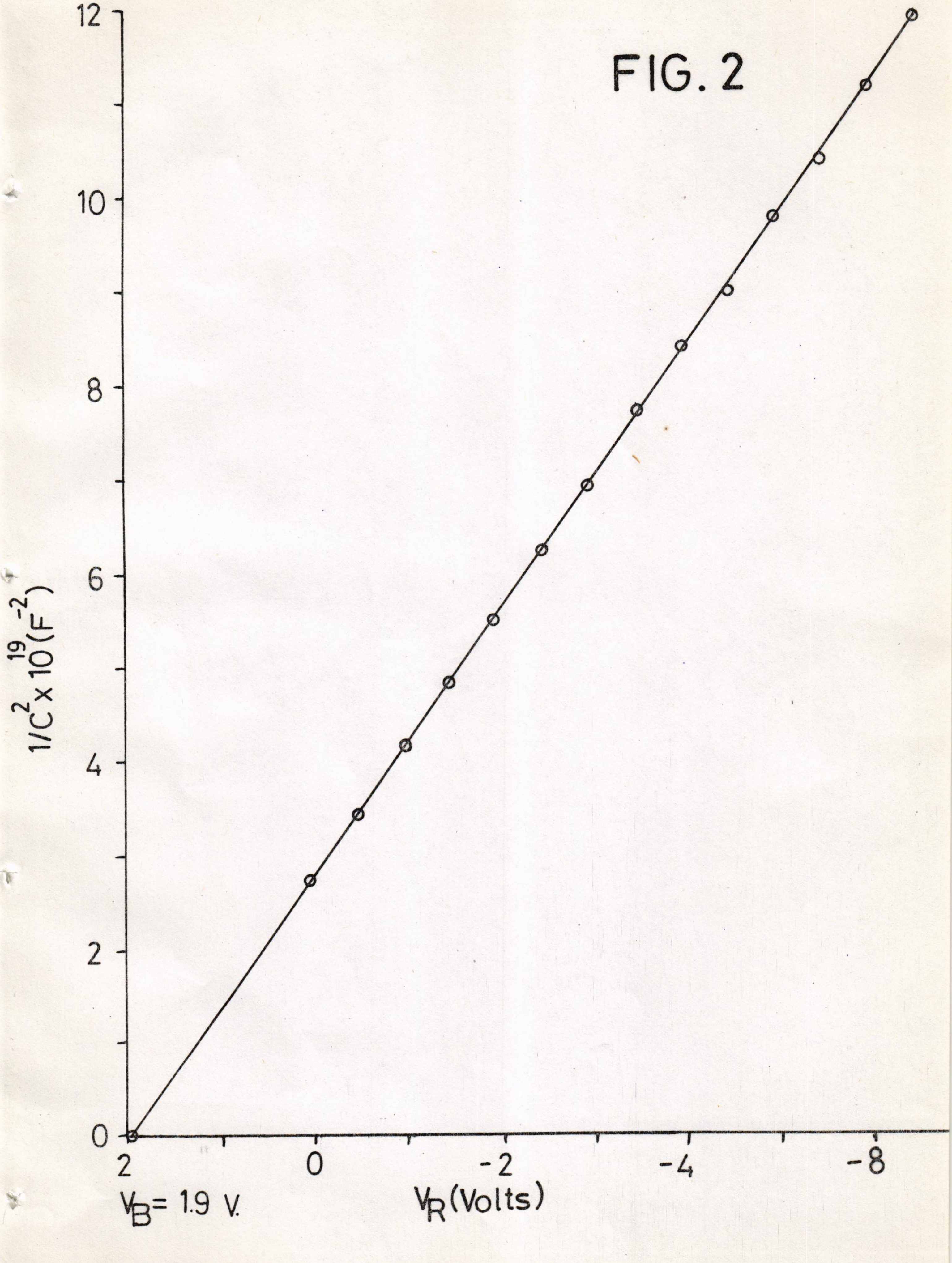
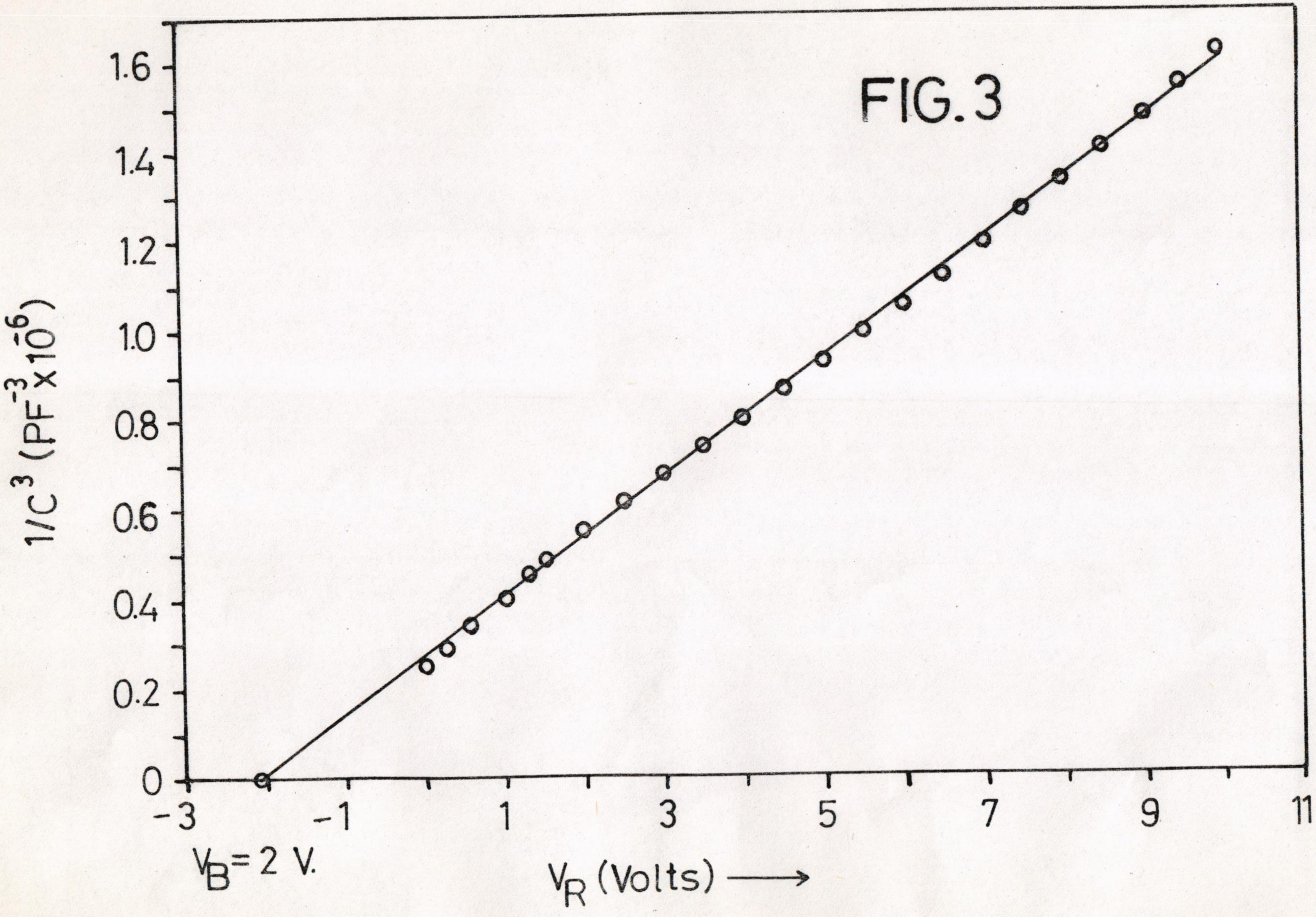

H3
E1
E2
E3
E5
DLTS Signal (arbitrary units)
0
4
8
12
14
Thermocouple Voltage (mV)

FIG.1

FIG. 2





$V_B = 2$ V.

FIG. 3

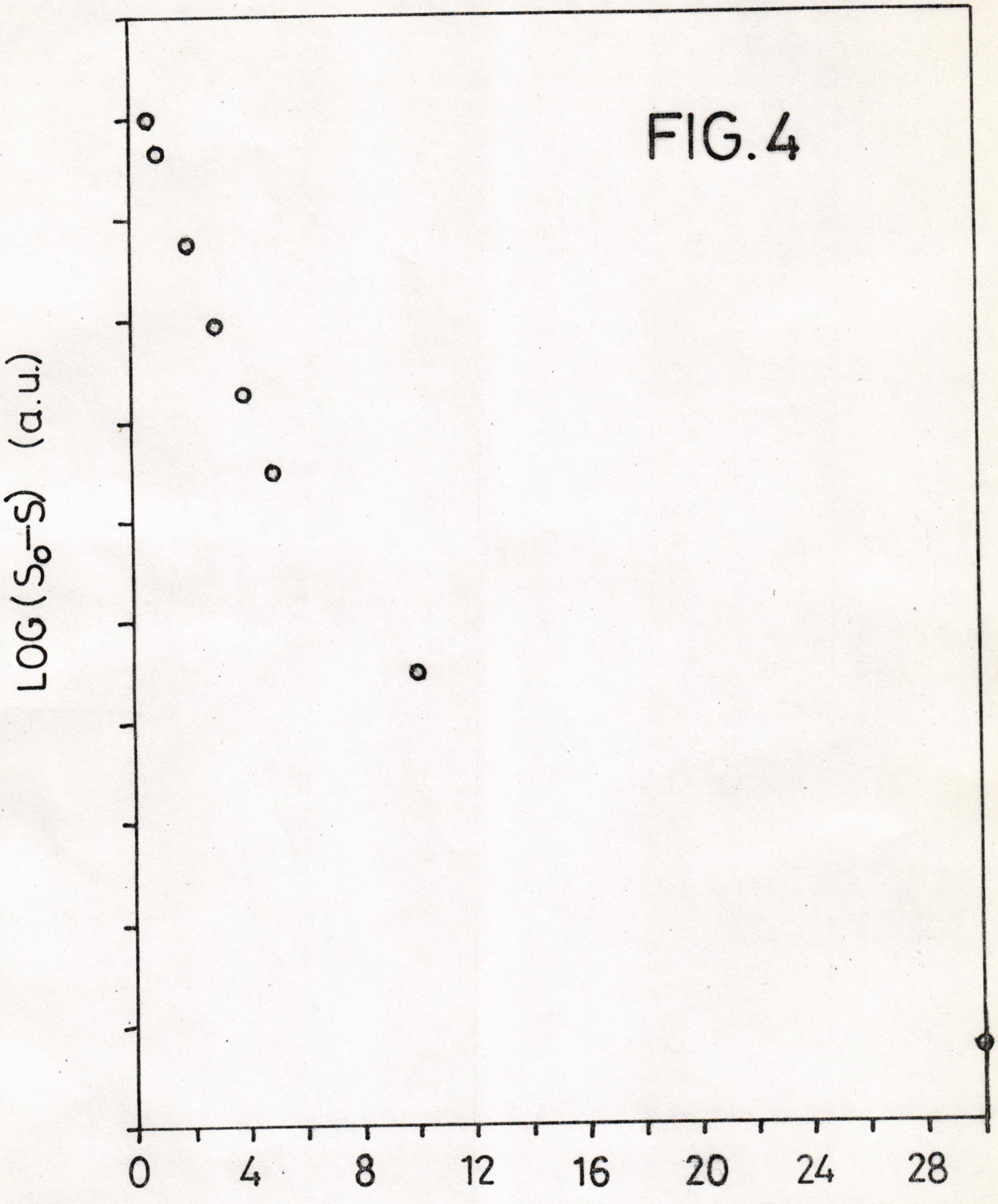


FIG. 4

Appendix I

Field effect on thermal emission from the 0.85-eV hole level in GaP

N. Baber and M. Zafar Iqbal
Semiconductor Physics Laboratory, Department of Physics, Quaid-i-Azam University, Islamabad, Pakistan

(Received 18 March 1987; accepted for publication 11 August 1987)

Results on the measurements of electric field dependence of thermal emission of holes from the 0.85-eV level in liquid-phase-epitaxial GaP, using deep-level transient spectroscopy, are reported for various temperatures. The observed field dependence is analyzed in terms of Poole–Frenkel emission from the three-dimensional Coulomb and square-well potentials. The field effect is found to be too weak to account for the large spread in the published emission rate data on the 0.85-eV hole level in GaP necessitating a reappraisal of its hitherto presumed origin.

I. INTRODUCTION

The electric field dependence of thermal emission of trapped carriers at deep-level centers in semiconductors has been both a source of concern and of important insight into the fundamental physics of the deep levels. Insofar as the emission rates are always measured inside the space-charge region of a semiconductor junction with an unavoidably high built-in field, one is always cautioned[1,2] against wrong information (activation energy and emission rates) being extracted from the emission rate data if proper account is not taken of the field effect. On the other hand, accurate measurements of the field enhancement of the emission rates lead to a model of the localized defect potential of the deep center thus providing vital insight into the nature of the defect states in the semiconductor crystal. Many such theoretical models based on a variety of forms of the potential wells associated with the defects have been developed,[3] some of which have been tested against experiment.

We report here investigations of the field effect on the 0.85-eV deep hole level in liquid-phase-epitaxial (LPE) GaP which is a commonly used material for the manufacture of light-emitting diodes (LED).

II. SAMPLES

p^+n junction green-emitting LEDs prepared by zinc diffusion in nitrogen doped n-type liquid-phase-epitaxial (LPE) GaP by Ferranti Ltd. (U.K.) have been used in this study. The doping concentration on the n-side has been found to be $\sim 10^{17}$ cm^{-3} from capacitance-voltage (C-V) measurements while the junction area is approximately 0.5×0.5 mm^2. The diodes are epoxy encapsulated after providing ohmic contact leads.

III. MEASUREMENTS

All measurements reported here are based on deep-level transient spectroscopy (DLTS) technique[4] using Metrimpex Semitrap DLS-81 lock-in-type detection system.[5] The samples were mounted on a TO-5 header in a variable temperature cryostat with a copper-constantan thermocouple mounted symmetrically to monitor the sample temperature to an accuracy better than 1°.

Following Lang,[2] a double pulse sequence of an injection (filling) pulse V_1 followed by a wide majority-carrier (clear) pulse V_2 was used so that the minority-carrier DLTS signal was obtained from a thin slice of the depletion region to ensure near uniformity of the electric field. The value of the electric field was varied by changing the standing reverse bias V_R on the junction. For each fixed reverse bias V_R, DLTS scans were performed with different emission rate settings as in the usual activation energy analysis, obtaining an Arrhenius plot for the T^2-corrected emission rates (e/T^2). The experiment was repeated for different values of V_R and from the resulting set of Arrhenius plots, curves were obtained for the emission rates versus electric field at several different temperatures spanning the range 350 to about 410 K. The average electric field in the thin slice of the depletion region from which the signal is obtained is calculated for each V_R from C-V measurements at the respective temperatures, using the standard formula for the field distribution in a step junction.

IV. RESULTS

A prominent minority-carrier (hole) emission peak has consistently been observed in our DLTS scans on all samples. The activation energy of the deep level corresponding to this peak is found to be ~ 0.85 eV, a typical Arrhenius plot for T^2-corrected emission rates being given in Fig. 1. This deep level is observed even with majority-carrier pulses both in DLTS as well as in single-shot capacitance transient experiments[6] due to the minority-carrier tails extending into the thin region adjacent to the metallurgical junction—a phenomenon discussed in detail by Meijer *et al.*[7] Of course, injection pulses greatly enhance the amplitude of this peak.

As recently pointed out[6] there is a very large (nearly three orders of magnitude) spread in the emission rates of the 0.85-eV hole level in GaP observed by various workers[8-13] (Fig. 2), causing serious controversy about the origin of this level which has hitherto been presumed to be the substitutional iron impurity.[8-10] This large spread could be interpreted in one of two ways:

(a) Various workers have observed the same center; one possible source [illegible] the wide spread could, in that case, be the high sensitivity of the emission to the junction electric field which could be different in the samples used by various

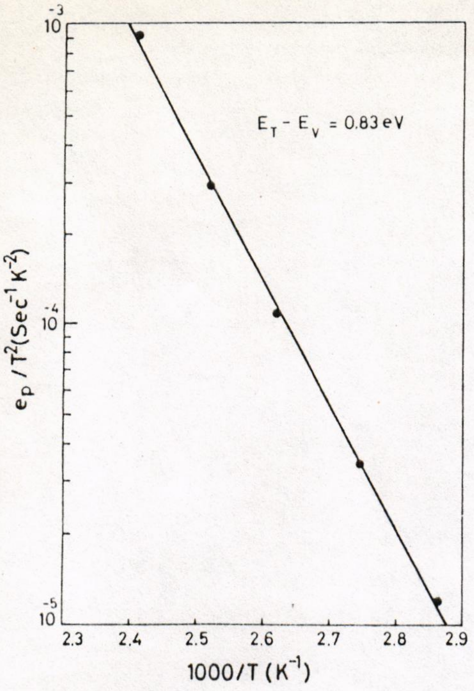


FIG. 1. A typical Arrhenius plot of the T^2-corrected emission rates for sample No. 2 obtained with $V_R = -2$ V, $V_1 = +1.1$ V, $V_2 = -0.5$ V.

workers depending on doping concentrations and junction fabrication techniques, etc.

(b) There are more than one 0.85-eV centers in GaP having the same activation energy but widely different emission rates.

While the knowledge of the field dependence of the emission rate is, per se, necessary to obtain insight into the nature of the 0.85-eV center, resolution of the above possibilities has been the primary motivating force for our detailed investigation of the field effect. The motivation is particularly strengthened by the fact that a similar large spread in the case of a 0.45-eV electron level in GaP appears to have been caused, at least partly, by the electric field.[14].

Using the double-pulse technique described above, data were obtained on the field dependence on a number of samples. Figure 3 shows such data on a typical diode for five different temperatures. Although there are variations over individual diodes, the emission rate is, in general, observed to increase by a factor of 3–5 as the field increases by a factor of about 3 corresponding to a variation in the junction reverse bias from 1 to 8 V. This enhancement is seen to be more or less independent of temperature, the emission rate increasing by almost the same factor with the electric field as the temperature increases from ~350 to ~410 K. We thus observe a finite but weak field enhancement of the hole emission rate from the 0.85-eV level.

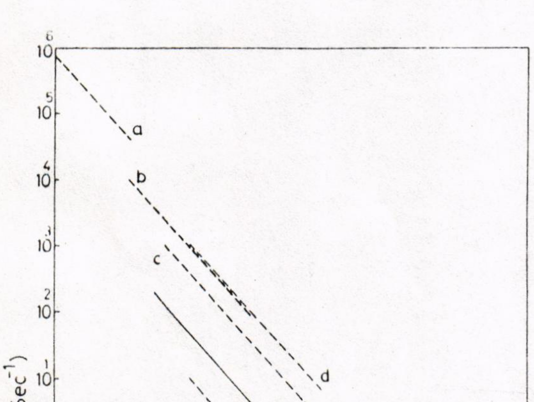


FIG. 2. Comparison of the published hole emission rate data for the 0.85 eV level: (a) Ref.11, (b) Ref.9, (c) Ref.7, (d) Ref. 10, (e) Ref. 12, and (f) typical data from our DLTS measurements.

V. THEORETICAL ANALYSIS

Theoretical models of electric field enhancement of thermal emission are based on the classical Poole–Frenkel effect and quantum mechanical tunneling through the potential barrier around the defect center. These calculations have been performed for a number of different model potential wells representing the defect center.[3] The earliest of these is based on Poole–Frenkel emission from a one-dimensional Coulomb potential well considered by Frenkel.[15] We have used the more realistic three-dimensional Coulomb potential Poole–Frenkel calculation presented by Hartke[16] and Jonscher,[17] for the analysis of our results. This calculation predicts a field enhancement in the emission rate given by

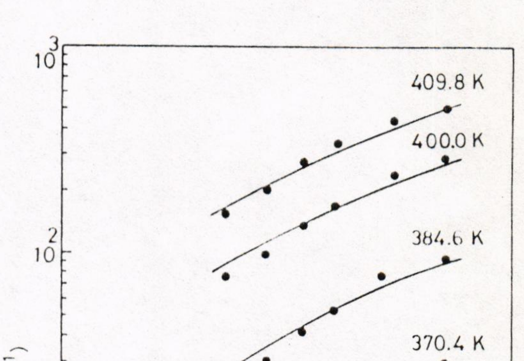


FIG. 3. Field dependence of the measured emission rates for sample No. 1 for the temperatures indicated. Solid circles represent measured data and the curves are theoretical fits based on the Poole–Frenkle model using three-dimensional Coulomb potential with $\epsilon_r = 10$.

$$e_p(E)/e_p(0) = (1/\gamma^2)[e^{\gamma}(\gamma - 1) + 1] + \tfrac{1}{2}, \qquad (1)$$

where

$$\gamma = (qE/\pi\epsilon_r\epsilon_0)^{1/2}(q/kT). \qquad (2)$$

Here e_p's represent the hole emission rates at the respective field strengths denoted by E, ϵ_r the relative permitivity of the semiconductor, ϵ_0 the permitivity of free space, and k the Boltzman constant, T being the temperature of measurement.

Using this expression we have computed the emission rate enhancement plotted as solid lines in Fig. 3. It can be readily seen that the three-dimensional Coulomb potential well models the 0.85-eV deep center very closely if Poole–Frenkel emission is assumed to be the dominant mechanism for the emission of holes. The value of ϵ_r used for this fit is the most quoted figure for the dielectric constant of GaP. The value of ϵ_r necessary to obtain good fits to data may however vary somewhat for different diodes. Fitting the data on another diode with this model, for example, requires a value of $\epsilon_r = 20$. Data for this diode are plotted on a linear scale for 351.1 K in Fig. 4 along with results for three-dimensional and one-dimensional Poole–Frenkel calculations for Coulomb potential well with $\epsilon_r = 10$ for comparison. It is clear that the one-dimensional calculation grossly overestimates the field enhancement, as is well known. A higher value of ϵ_r required for the fit to data in the three-dimensional case would seem to imply a screening effect on the Coulomb potential which might vary from diode to diode (e.g. because of shallow dopant concentration variation, etc.).

As it is common to associate non-Coulombic potentials with deep level centers, we may add here that we have also investigated the possibility of fitting our data with Poole–Frenkel emission from a square-well potential which gives

$$e_p(E)/e_p(0) = 1/(2\beta)(e^{\beta} - 1) + \tfrac{1}{2}, \qquad (3)$$

where

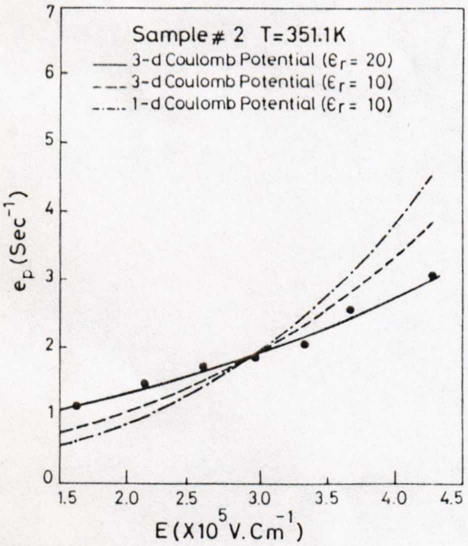


FIG. 4. Typical field dependence data for sample No. 2 (solid circles) compared with calculations based on one-dimensional and three-dimensional Poole–Frenkel models with Coulomb potential (curves). Three-dimensional Coulomb potential gives good fits with $\epsilon_r = 20$ for this sample for other temperatures as well.

$$\beta = qEr_0/kT. \qquad (4)$$

Here r_0, the width of the square well, is a free parameter. We find best fits to our data for values of r_0 ranging from 21 to 30 Å. These fits are shown in Fig. 5, for the same two diodes for which data have been presented in Figs. 3 and 4. As seen in the figure, although the fits are reasonably good, the data for sample 1 does not fit as well with the theoretical curve as that for sample 2.

VI. DISCUSSION

It is clear from the above that the weak observed field dependence of the hole emission from the 0.85-eV level in LPE GaP can be well described by the Poole–Frenkel barrier lowering due to the electric field if one associates a three-dimensional Coulomb potential well with the center, although a square-well potential also describes the data reasonably well. A Coulombic well is, of course, physically more appealing than the rather artificial non-Coulombic square well, although a clear choice between the two would require data over a much larger span of field variation which is not realistically feasible due to limitations posed by junction breakdown.

The Coulomb potential is, of course, characteristic of a point charge which would imply that the hole emission process from the 0.85-eV level takes place from a charged center. So if the Coulombic-potential description is adopted for this center one would expect the 0.85-eV level to originate from an acceptorlike center which is negatively charged after emitting a hole while adoption of the square-well potential model would imply it being neutral. It may be of interest to note that a three-dimensional Poole–Frenkel model with Coulomb potential has also recently been shown to yield a good description of thermal emission from two donorlike centers in silicon by Irmscher *et al.*[18] In contrast to other

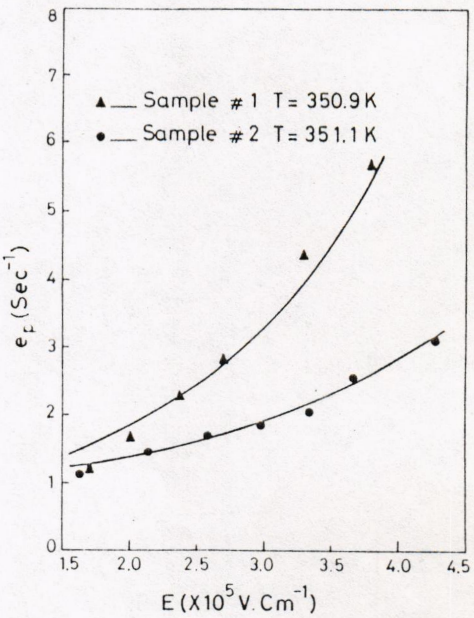


FIG. 5. Typical field dependence data for samples No. 1 and 2 compared with calculations based on the Poole–Frenkel model using square-well potential (solid curves). The well width r_0 is 21 Å for the lower curve and 30 Å for the upper curve.

deep-level systems such as Cr[19] and EL2[20] in GaAs, no additional contribution of the phonon-assisted tunneling seems to be needed to model the field dependence in our case or in the case of Irmscher *et al.*[18] The phonon-assisted tunneling has been shown to give a far stronger field enhancement effect by Makram-Ebeid and Lannoo.[3]

As regards the basic motivation of this work, it is clear that the observed field dependence of the hole emission is too weak to account for the spread in the observed emission rates reported by various workers in the case of the 0.85-eV level in GaP. It would, therefore, be highly unlikely that these data relate to the same center. It is our opinion that the data from various workers represent more than one center in GaP giving rise to deep levels with the activation energy of 0.85 eV but having different emission rates. It is interesting to note in this context that a literature survey indicates at least two candidates for the 0.85-eV hole level, namely, substitutional iron impurity[8–10] and $Zn_{Ga}V_P$ (zinc-vacancy) complex.[11] While the latter reference challenges the earlier strong evidence in favor of the iron impurity, in the light of the above discussion it seems likely that both these defects (and perhaps more) may be responsible for the 0.85-eV hole level rather than one or the other exclusively.

VI. CONCLUSIONS

Thermal emission of holes from the 0.85-eV center in LPE GaP has been found to be weakly field dependent. It has been shown that the observed field enhancement can be well described in terms of Poole–Frenkel emission from a Coulomb potential well associated with the center which may be screened to some extent. This leads one to infer that the deep level in question arises from a charged (acceptorlike) defect center. However, the association of a square-well potential with the center (neutral in that case) cannot be ruled out. This study strengthens the possibility of more than one 0.85-eV deep hole centers in GaP.

ACKNOWLEDGMENTS

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APPENDIX II

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CAPTURE CROSS-SECTIONS OF THE 0.45 eV LEVEL IN GaP

N. Baber and M. Zafar Iqbal

Semiconductor Physics Laboratory, Department of Physics
Quaid-i-Azam University, Islamabad, Pakistan

A deep level at E_c-0.45 eV is always found in N-doped GaP. A large discrepancy in its electron capture cross-sections (σ_n) is found in literature. To remove this discrepancy we have investigated the temperature dependence of σ_n using Deep Level Transient Spectroscopy (DLTS). σ_n is found to decrease exponentially with inverse temperature with a large activation energy for electron capture (~0.24 eV). The extrapolated σ_n at $T = \infty$ is unusually large (~10^{-12} cm^2),compared with the predictions of the multiphonon capture model of Henry and Lang.

The carrier capture cross-section is an important property of deep electronic levels lying within the band gap of a semiconductor. These cross-sections are known to provide insight into the physics of these defect levels [1,2]. In this report we present results of electron capture cross-section (σ_n) measurements on a level which is always found in Nitrogen-doped GaP. A number of reports [3-7] have found the activation energy for the thermal excitation of an electron from this level to the conduction band to be around 0.45 eV. The σ_n values reported in these studies vary widely, from 10^{-17} cm^2 to 10^{-12} cm^2. To remove this discrepancy we have investigated the temperature dependence of σ_n for this level.

The samples used were green light-emitting diodes (LED) manufactured by Ferranti Ltd. (UK). These were p^+n junction diodes prepared by zinc diffusion in n-type liquid-phase-epitaxial GaP doped with nitrogen. The background doping concentration on the n-side, as measured from C-V characteristics, was ~ $5x10^{16}$ cm^{-3}. The measurements were done using deep level transient spectroscopy (DLTS) technique[8] with excitation pulses as short as 30 ns.

A typical Arrhenius plot for the emission rate data obtained from DLTS for the level studied is given in Fig.1. The emission

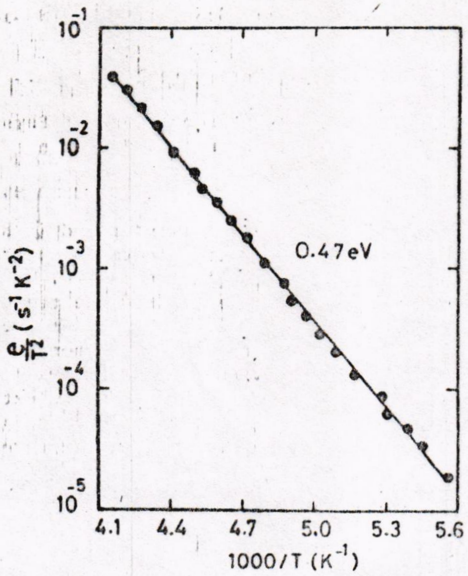

Fig.1. Arrhenius plot of T^2-corrected emission rate data

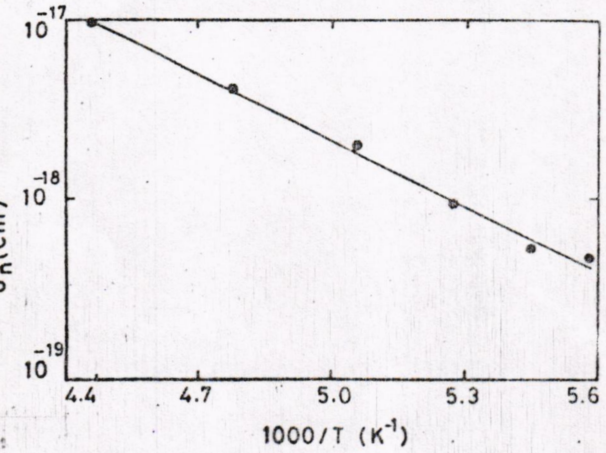

Fig.2. Temperature dependence of the electron capture cross-sections obtained from DLTS measurements

activation energy (E_a) and the concentration of the deep level are found to be 0.47 eV and $\sim 5\times10^{13}$ cm^{-3}, respectively.

The electron capture cross-sections σ_n obtained from DLTS measurements of the capture rates in the standard manner [1,8], at different temperatures, are plotted in Fig.2. Clearly σ_n is seen to vary with temperature according to

$$\sigma_n = \sigma_\infty \exp(-E_\sigma/kT) \qquad (1)$$

where σ_∞ is the capture cross-section at $(1/T)=0$ and E_σ is the activation energy for capture. The slope of the least-square straight line fit to the data points gives $E_\sigma = (0.24\pm0.02)$eV. Thus the "true" thermal energy depth of the level below the conduction band edge would be $E_T = E_a - E_\sigma = (0.23\pm0.02)$eV. The extrapolated σ_∞ from Fig.2 is 3×10^{-12} cm^2. This value is in general agreement with the extrapolated value of $\sigma_\infty = 5\times10^{-13}$ cm^2 obtained from the detailed balance analysis [1] of the emission rate data of Fig.1 considering the large errors usually inherent in the latter evaluation.

The exponential dependence of σ_n on 1/T reported here resolves most of the discrepancy reported in earlier works [3-6] except for the work of Ferenczi et al [7] in which it is inferred that $\sigma_n > 10^{-16}$ cm^2. However, since this report does not mention the temperature of measurement, it is difficult to compare our results with it with certainty.

The exponential decrease of σ_n with 1/T that we have observed for this level is characteristic of capture by multiphonon emission (MPE) process modelled by Henry and Lang [2]. Their paper, however, predicts, $\sigma_\infty \approx 6\times10^{-15}$ cm^2 and most of the levels in GaAs and GaP that have been reported to exhibit capture through MPE have been found to have σ_∞ between $10^{-14} cm^2$ and 10^{-15} cm^2. A few exceptions exhibit σ_∞ on the lower side (e.g. σ_n of Oxygen State 2 in GaP [2]). Our value of $\sigma_\infty = 10^{-12}$ cm^2 is one of the highest ever reported capture cross-section values.

The capture activaion energy ($E_\sigma = 0.24$ eV) is a rather large fraction of the thermal emission activation energy ($E_a = 0.47$ eV). Such energies are typical of the so called DX centres commonly found in compound semiconductors. It has been reported [3,4,7] that the concentration of the 0.45 eV level is related to both donor and nitrogen impurity concentrations. However, the large capture cross-sections of the 0.45 eV level that we have found are unlike those of the typical DX centres which are known for their extremely small caputre cross-sections. No DX centre has been clearly identified in GaP. It is tempting to speculate that the 0.45 eV level in N-doped GaP is some kind of a counterpart of a DX complex in GaP involving nitrogen, which retains the feature of large capture barrier height E_{σ} while having large capture cross-section not typical of DX centres. Clearly, further detailed investigations such as ENDOR will be needed to reveal the microscopic structure of the centre.

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APPENDIX III

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TRANSIENT CAPACITANCE MEASUREMENTS ON A MID-GAP DEEP LEVEL IN GaP

A.Ali, N.Zafar and M.Zafar Iqbal
Semiconductor Physics Laboratory
Department of Physics
Quaid-i-Azam University
Islamabad,Pakistan.

ABSTRACT:

High temperature transient capacitance measurements on green-emitting liquid-phase-epitaxial GaP p$^+$n junctions are reported. A mid-gap electron level is found to be present in significant concentrations (10^{14} - 10^{15} cm^{-3}). The emission characteristics of this level have been studied over a wide range of temperatures. Detailed results on emission rate data and activation energy are presented.Preliminary measurements indicate an electron capture cross-section $\sim 7\times10^{-20}$ cm^2.

I. INTRODUCTION:

In spite of over a decade of intensive research the problem of the dominant non-radiative 'Killer' centre in GaP remains unsolved. The extremely poor light emission efficiency of Nitrogen doped green emitting GaP LEDs (light emitting diodes) is generally ascribed to some, as yet undiscovered, deep level providing an efficient non-radiative shunt path for electron-hole recombination. This research, although failing to provide a definite answer as to the single most important 'Killer' centre, has nevertheless led to the detection and characterization of a number of possible deep level candidates.

We report here measurements on mid-gap deep level in Nitrogen doped (GaP recently detected in our studies. We consider this a particularly important finding since according to the well established Shockley-Read-Hall theory[1], mid-gap deep level centres are known to be the most efficient recombination centres in semiconductorss.

II. MATERIAL:

p$^+$n junction green-emitting LED's prepared by Zinc diffusion in Nitrogen doped n-type liquid-phase-expitaxial(LPE) GaP by Ferranti Ltd. (U.K.) have been used in this study. The doping concentration on the n-side has been found to be $\sim$ 1017 cm^{-3} from capacitance-voltage (C-V) measurements while the junction area is approximately 0.5 mm x 0.5 mm. The diodes are epoxy encapsulated after providing ohmic contact leads.

III. EXPERIMENTAL DETAILS:

To obtain a first information on the deep level content of our samples the thermally stimulated capacitance (TSCAP)[2] technique was used. Here the samples are cooled with no applied bias to fill the deep levels and subsequently heated at a slow rate after applying a reverse bias to observe thermal emission at a characteristic temperature. A sharp capacitance step arises due to emission at this temperature which can be analysed to obtain an estimate of the deep level activation energy[2].

The bulk of the results reported here relate to the thermal emission characterization of the mid-gap centre. Such data are thought to provide a 'signature' of a deep level. For these data to provide a reliable signature, emission rates should be measured over as wide a range of temperature as possible. Although the now popular deep level transient spectroscopy (DLTS) technique[3] can be conveniently used to provide such data, the range of (temperatures) this technique is often limited to 1-2 orders of magnitude of the emission rate for most practical set-ups. In the case of our mid-gap level this range was even more limited (to hardly one order of magnitude) due to the prohibitively high temperatures involved for higher rate windows. In order to extentd this range, therefore, we have combined the DLTS technique and the single-shot dark capacitance transient measurements. This enabled us to extend the data to nearly four decades in the emission rate.

DLTS signals were measured 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 of 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.

For the single-shot capacitance transient measurements the stability of the sample temperature is of utmost importance. This was achieved by mounting the sample in a different high thermal mass home-built cryostat used with an electronic temperature controller. The temperature stability obtained with this set-up was better than 0.1 degree. The transients were obtained by switching the junction diode bias from zero to reverse(typically 5 volts) and monitoring the capacitance with a Boonton 72B capacitance Meter with output connected to a chart recorder while the sample was maintained at a constant temperature. Rising capacitance transients with time constants ranging from a few seconds to a few hours were observed and recorded. These measurements were carried out at temperatures ranging from ~330 K to ~430 K where the time constants became inconveniently long.

IV. RESULTS:

The mid-gap level was first detected[4] in our TSCAP scans intended to obtain general information on the deep level content of the green-emitting LEDs. Typical TSCAP scans at four different heating rates are shown in Fig.1. A significantly large TSCAP step is clearly seen in these scans which shifts to higher temperatures with increasing heating rate. Measurements of this shift can be analysed to obtain an approximate value of the thermal activation energy as suggested by Buehler[2] for instance. Such an analysis is

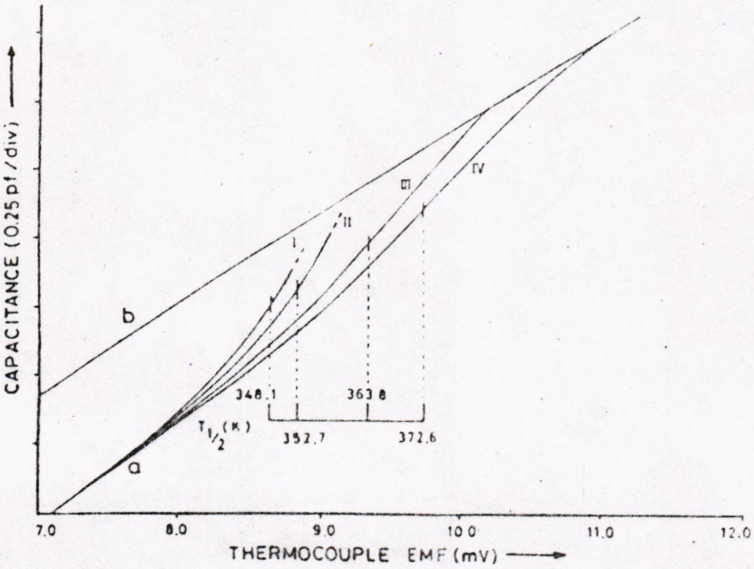

FIG.1. Recorder traces showing
(a) TSCAP steps corresponding to heating rates $\beta_{\frac{1}{2}}$=0.40(I), 0.74(II), 2.52(III) and 5.76(IV)degrees/minute. The temperature $T_{\frac{1}{2}}$ are marked on each curve.
(b) Capacitance variation for the trap empty case
A reverse bias of 7V was used during heating for both(a) and (b).

presented in Fig.2 giving an activation energy of 1.09 ±0.03 eV for the deep level observed placing it at almost mid-gap position in the band gap of GaP. Subsequently we observed a pronounced peak in

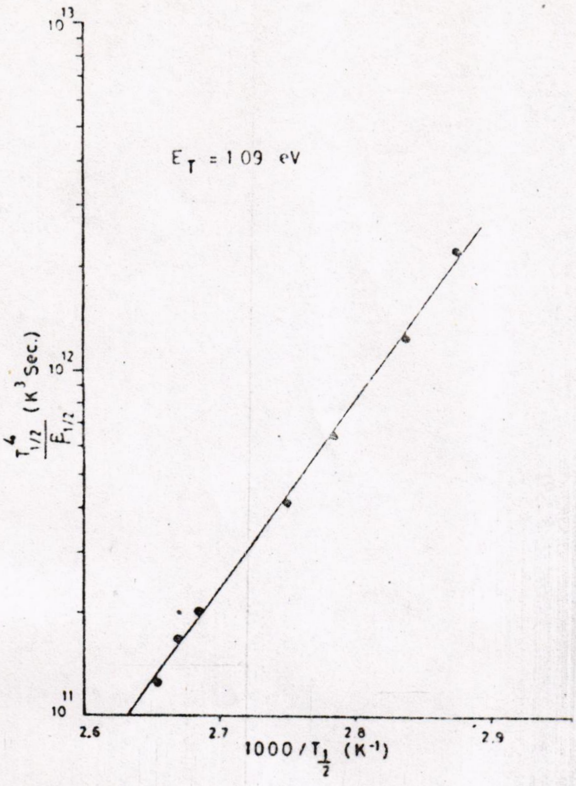

FIG.2. $\ln(\frac{T^4_{\frac{1}{2}}}{\beta_{\frac{1}{2}}})$ vs. $\frac{1000}{T_{\frac{1}{2}}}$ plot giving the thermal activation energy of the deep level.

our DLTS spectra corresponding to this level by extending our DLTS measurements to the exceedingly high temperatures. A typical DLTS peak corresponding to this level is displayed in Fig.3. The highest emission rate window used by us in DLTS on this level is 2.26 sec^{-1} which gives a peak at ~ 475 K which is just about the highest temperature advisable for the safe measurements on GaP LEDs. The lowest practical emission rate window allowed by our deep level spectrometer is 0.1 sec^{-1} which means that we could only obtain the DLTS spectra for the mid-gap level over a decade of emission rates.

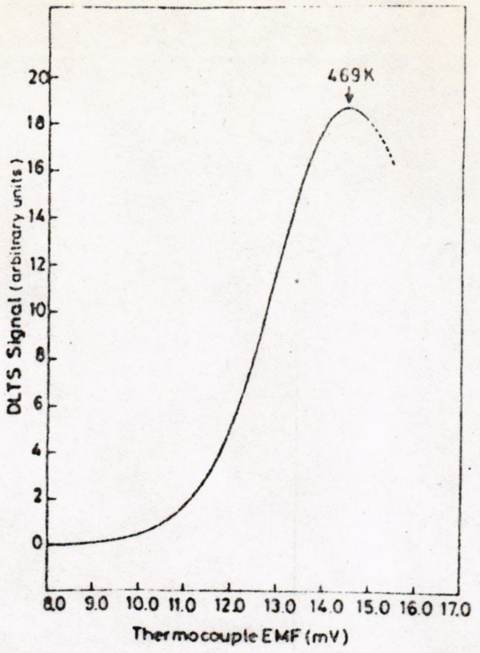

FIG. 3. DLTS peak obtained with 1.13 sec^{-1} rate window.

Single-shot capacitance transient measurements allowed us to extend this range by working at lower temperatures. A typical full transient plotted as log(ΔC) vs. time is shown in Fig. 4. The full

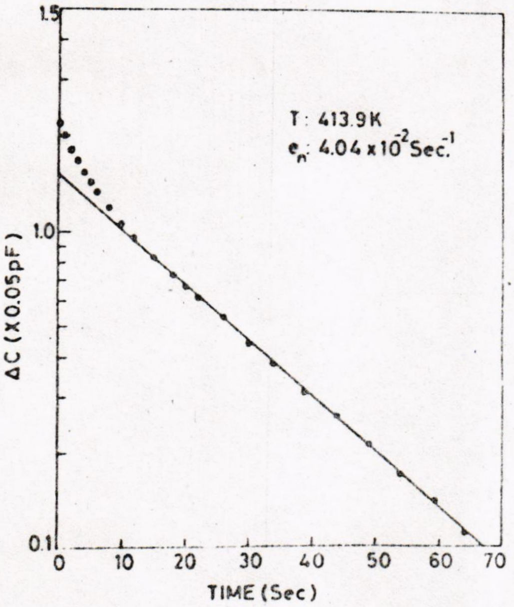

FIG. 4. Typical single-shot dark capacitance transient.

transient is clearly non-exponential in general describable as sum of of two exponentials. This suggests electron emission from at least two distinct levels at these temperatures. The second, long time part of the transient was found to give time constants (emission rates)which agreed very closely with the DLTS emission rates at similar temperatures. It was thus established that the second exponential part of our transients is caused by emission from the mid-gap level. Consequently detailed emission rate data were obtained for the mid-gap level from the slopes of the second(long time) part of the log ΔC vs. t plots of the transients obtained over a wide range of temperatures down to 330 K below which measurements were cumbersome due to exceedingly slow transients. These emission rate data alongwith the DLTS results are shown in Fig.5

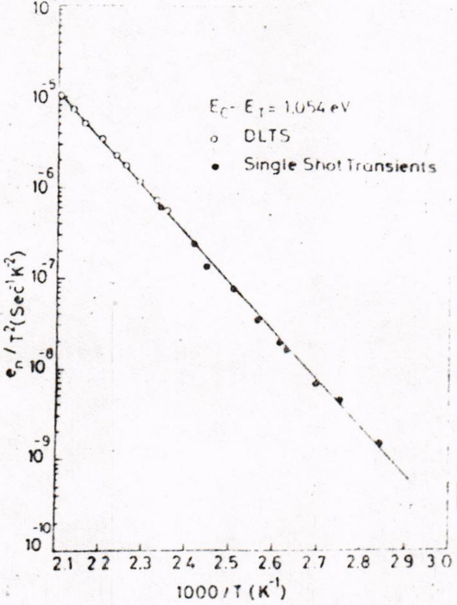

FIG.5. Typical Arrhenius plot of T^2-corrected emission rate obtained using DLTS and single-shot measurements.

which is the Arrhenius plot of the T^2 -corrected emission rates for a typical diode. The activation energy is found to be 1.05 eV which is more accurate than,but in general agreement with,the value of 1.09 ± 0.03 eV obtained from TSCAP measurements. Arrhenius plot of Fig.5 thus provides a signature of the mid-gap level. This deep level was found in significantly high concentrations for an inadvertent defect which varied from $\sim 1.5 \times 10^{14}$ to $\sim 10^{15}$ cm^{-3} over the devices studied.

We have also carried out preliminary investigations of the electron capture cross-section of this level using the conventional DLTS and the differential DLTS(DDLTS) techniques. The preliminary results indicate a capture cross-section ~7 x 10^{-20} cm^2 for this level at ~465 K.

V. DISCUSSION:

The deep [illegible] observed by us seems to be one of the deepest native defects ever observed in LPE GaP. Comparison of the activation energy with published results indicates the following possible candidates:

Oxygen[5]	state 1	1.18 eV
	state 2	1.08 eV
Deep level induced by current stressing(thought to be P_{Ga})[6]		1.18±0.05 eV
P_{Ga} antisite[7] (from photo-EPR)		1.10±0.10 eV
D5[8]		1.03 eV
D6[8]		1.06 eV

Our samples contain no intentional oxygen - any inadvertent oxygen would not be expected to be present in such high concentrations as observed in our experiments. Further non-observance of any strong DLTS peak at similar temperatures in oxygen doped red-emitting GaP LEDs in our investigations would seem to rule out the possibility of identifying our mid-gap centre with oxygen. The deep donors D5 and D6 observed in MOVPE (metal-organic vapour phase epitaxy) GaP[8] have very different emission rates as compared to our 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 as measured by Ferenczi etal for the deep level attributed to P_{Ga} in their forward current stressing experiments are somewhat smaller than our measured values. However, in view of their admittedly poor data over very limited temperature range, it is possible that this discrepancy between our two 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 analogue of the well known EL2 (in GaAs) centre in GaP. Clearly further work will be needed to establish the identity of the mid-gap centre detected by us definitively.

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APPENDIX IV

Electrical characterization of inadvertent midgap levels in GaP

M. Zafar Iqbal, Asghar A. Gill, and N. Baber
Semiconductor Physics Laboratory, Department of Physics, Quaid-i-Azam University, Islamabad, Pakistan

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Results of an electrical characterization study of two hitherto unobserved midgap deep levels in GaP using deep-level transient spectroscopy and single-shot dark capacitance transient techniques are reported. These are the dominant majority-carrier (electron) levels in the green-light-emitting diodes studied. Detailed electron emission rate and capture cross-section measurements are performed on these levels. The shallower of the two levels is found to have an activation energy to the conduction band varying from 0.88 ± 0.02 eV to 0.93 ± 0.02 eV from sample to sample while the activation energy of the deeper level is 0.96 ± 0.02 eV. The results of the capture measurements give an upper limit of 1.2×10^{-19} cm^2 for the electron capture cross sections of the two levels. A detailed comparison of the emission rate data with the published results on midgap levels in GaP is presented. It is proposed that one of these midgap levels may be the counterpart in GaP of the well-known EL2 level found in GaAs.

I. INTRODUCTION

Midgap deep levels have enjoyed a special status in semiconductor physics and technology ever since Shockley and Read[1] and Hall[2] first pointed out their role as most efficient recombination centers on the basis of kinetic considerations. The gold acceptor in Si and EL2 in GaAs are prominent examples which have attracted a lot of attention of physicists and technologists alike. The midgap electron level EL2 in GaAs has been the subject of extensive research and still lacks a comprehensive and definitive understanding in spite of over a decade of intense investigations. One interesting approach to the understanding of the systematics of EL2 behavior has been the attempt to track this deep level in the entire $GaAs_{1-x}P_x$ alloy system from one stoichiometric extreme, $x = 0$ (GaAs), to the other $x = 1$ (GaP).[3,4] This brings into sharp focus the search for midgap levels in GaP which may be possible counterparts of EL2. This study is also motivated by the fact that midgap levels can act as efficient nonradiative recombination centers in semiconductors. As such, their characterization is necessary to identify the "killers" of the luminescence efficiency of light-emitting diodes (LEDs), which is known to be particularly low in green LEDs of GaP.

We had earlier reported[5] the presence of an inadvertent midgap level in liquid-phase-epitaxial GaP using a thermally stimulated capacitance (TSCAP) technique which yielded an activation energy of 1.09 ± 0.03 eV. Here we report detailed investigations of the midgap levels in this material using the complementary techniques of deep-level transient spectroscopy (DLTS)[6] and single-shot isothermal capacitance transients.[7] These measurements reveal the presence of two midgap deep levels situated energetically close to one another in the band gap. This report aims to present detailed thermal emission and capture characteristics of these two levels.

II. EXPERIMENTAL DETAILS

A. Material and samples

The p^+n junction, green-emitting LEDs prepared by zinc diffusion in nitrogen-doped, *n*-type, liquid-phase-epitaxial (LPE) GaP were fabricated by Ferranti Ltd. (U.K.). The doping concentration on the *n* side has been found to be $\simeq 10^{17}$ cm^{-3} from capacitance-voltage (*C-V*) measurements. The junction cross section is 0.5×0.5 mm^2. After application of ohmic contact leads, the diodes were encapsulated in epoxy.

B. Emission rate measurements

For single-shot dark capacitance transient measurements the samples were mounted in a homemade, finger-type cryostat used with an electronic temperature controller. The temperature stability obtained with this setup was better than 0.1 K. The transients were obtained by switching the diode bias from zero to reverse (typically 5 V) and monitoring the capacitance with a Boonton 72B capacitance meter with output connected to a chart recorder, while the sample was maintained at a constant temperature. Rising capacitance transients with time constants ranging from a few seconds to a few hours were recorded. These measurements were carried out at temperatures ranging from ~330 to ~430 K.

DLTS signals were measured using a Metrimpex DLS-81 deep-level spectrometer based on the lock-in principle.[8] This DLTS setup could also be used in the differential DLTS mode,[9] which was employed for capture measurements as explained in Sec. II C. The samples were mounted in a variable temperature cryostat with a copper constantan thermocouple mounted symmetrically with respect to the sample to monitor the temperature. Temperature accuracy of better than 1 K could be attained with this arrangement. Excitation of the deep levels was performed by using reduced-bias, majority-carrier pulses.

C. Capture cross-section measurements

The standard method for such capture measurements[10,11] is to fill the deep levels partially by using DLTS excitation pulses of width (duration) t_p much smaller than the capture time constant of the level. As t_p is increased, the corresponding DLTS peak height S increases, finally saturating to some value S_0 for long enough t_p when all the levels

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are filled. A plot of $\ln(S_0 - S)$ vs t_p obtained from such measurements is supposed to yield a straight line whose slope is expected to provide the capture time constant.

We have, however, for the most part used the differential DLTS mode which is expected to provide a more accurate method for such capture measurements. In this mode, the sample is excited by two successive pulses of equal height but different durations. The DLTS output gives the difference between the capacitance transient signals resulting from the two pulses.[9] The width of the first pulse is kept at the saturation value while the width of the second pulse t_p is varied. The resulting DLTS peak height, which then gives $(S_0 - S)$ directly, decreases with an increase in t_p.

III. RESULTS

A. Emission rate measurements

The DLTS measurements reveal a dominant majority-carrier peak in all the samples. Figure 1 shows this peak in a typical DLTS spectrum. The highest emission rate window used was 2.26 s^{-1} giving a peak at ~475 K, which is just about the highest temperature advisable for safe measurements on the samples used. The emission rate data obtained from DLTS spectra are plotted in Fig. 2 as open circles.

A typical isothermal dark-capacitance transient is plotted in Fig. 3 (open circles). The transient is in general nonexponential. The long-time part clearly follows a single exponential. The short-time data, corrected after subtracting the contribution of the deeper level obtained from the extrapolated part of this straight line, are replotted as solid circles in the same figure. This corrected short-time part of the transient is also seen to follow a straight line on this semilog plot. The capacitance transients are thus found to follow a sum of two exponentially rising signals corresponding to emission of majority carriers (electrons) from two distinct deep levels. The emission rates for the two levels are obtained from the respective time constants inferred from the slopes of the corresponding straight line fits computed using least-squares analysis. The experiment is repeated at a number of fixed temperatures to obtain emission rates of the two deep levels at different temperatures. The emission rate data obtained from such experiments for the short-time and long-time parts are shown in Fig. 2 as filled squares and filled circles, respectively.

As can be seen from Fig. 2, the emission rates obtained from DLTS measurements agree well with the emission rates corresponding to the long-time part of the single-shot

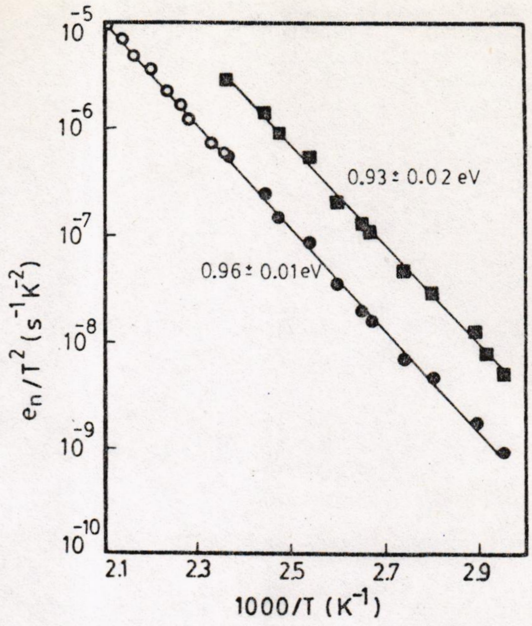

FIG. 2. Thermal emission rates (e_n) data for the two levels obtained from DLTS (open circles) and single-shot measurements (filled circles from long-time data and squares from short-time data).

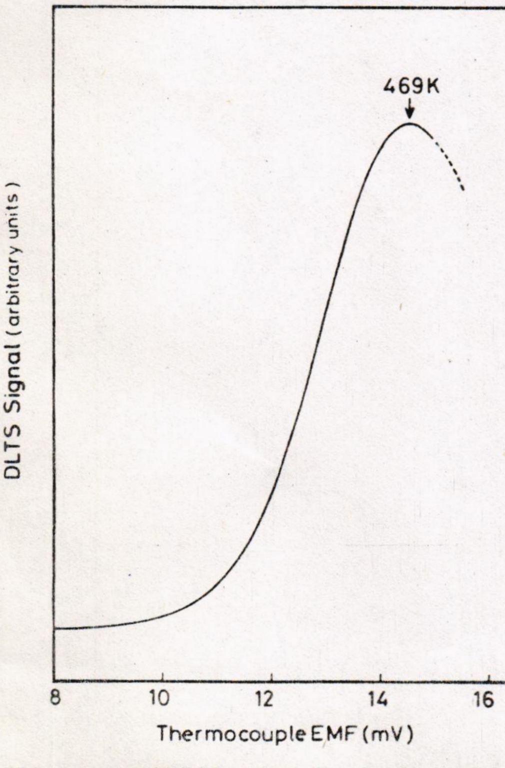

FIG. 1. A typical DLTS spectrum showing the dominant majority-carrier (electron) peak. $e_{\max} = 1.13\ \text{s}^{-1}$, $V_R = -6$ V.

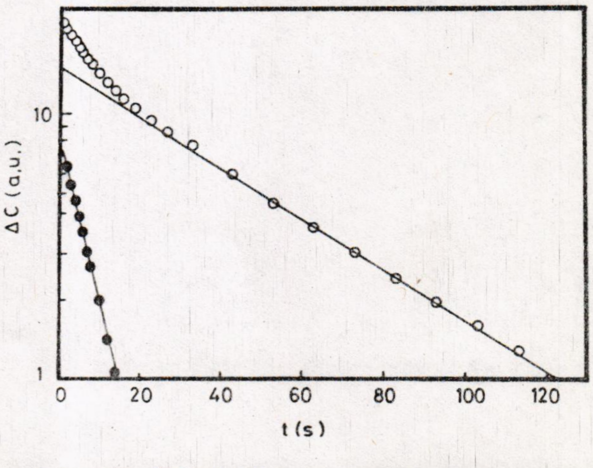

FIG. 3. Typical single-shot dark capacitance transient (open circles). The filled circles were obtained by subtracting the contribution of the long-time exponential part.

capacitance transients. The short-time part of the single-shot transients is seen to correspond to a distinctly different deep level. From single-shot measurements, it is found that the two deep levels have concentrations in the range 10^{14}–10^{15} cm^{-3}, varying from sample to sample. In general, the concentration of the deeper level is observed to be roughly twice that of the shallower level. The observation of a single DLTS peak instead of two was initially a somewhat unexpected finding. However, our computer simulations of the DLTS line shape based upon the singe-shot emission rate data reveal that, for such relative concentrations of the two levels, the DLTS peak shape indeed corresponds to that given in Fig. 1.

Thus, the single-shot, dark-capacitance, transient data show the presence of two near midgap levels while the DLTS is unable to resolve the two, showing a single peak in the investigated temperature range. This highlights the importance of the single-shot method as a complementary technique. The use of the two techniques seems to be essential not only for extending the range of emission rate data but also for convincingly resolving two deep levels having similar activation energies.

The Arrhenius plot of Fig. 2 provides the activation energies of the two deep levels investigated. The lower straight line gives an activation energy $(E_c - E_t) = 0.96 \pm 0.02$ eV while for the upper straight line $(E_c - E_t)$ varies from 0.88 ± 0.02 eV to 0.93 ± 0.02 eV from diode to diode.

B. Capture cross-section measurements

We have also attempted to measure the electron capture cross sections using DLTS. The results of capture measurements using the differential DLTS method discussed in Sec. II C are presented in Fig. 4. As mentioned there, the plot of $\log(S_0 - S)$ vs t_p is expected to be a straight line, the slope of which would give the capture time constant. However, the data do not fall on a straight line. This is only to be expected since, as our single-shot measurements show, the DLTS peak is not due to a single deep level. The curve does not seem to fit with a sum of two exponentials either. This is most likely caused by the capture effects from carrier tails[12] from the two levels which make the long-time capture nonexponential even when the signal is due to one level alone. Thus, the capture rates of the two levels obviously cannot be clearly resolved. However, the slope of the short-time part of the curve in Fig. 4 gives the upper limit to the capture cross sections of the two levels. This is found to be $1.2 \times 10^{-19}\ \mathrm{cm}^2$ at $T = 465$ K.

It might be pointed out that the capture cross section can also be estimated indirectly at $1/T = 0$ from the intercept of the Arrhenius plot[11] of Fig. 2. In our case, for the shallower level, this gives a value for the cross section of $(5 \pm 2) \times 10^{-21}\ \mathrm{cm}^2$, and for the deeper level, 6×10^{-21} cm^2. In view of the large errors usually inherent in such an evaluation, these values would seem to be in general agreement with the upper limit obtained from direct measurements given above.

IV. DISCUSSION

In an attempt to identify the origin of the two levels observed, we have compared the emission rate signatures of the two levels observed in the present work with those of the previously reported midgap electron levels in GaP. Such a detailed comparison is presented in Fig. 5. As can be clearly seen, the levels D_5 $(\Delta E \equiv E_c - E_T = 1.0\ \mathrm{eV})$ and D_6 $(\Delta E = 1.06\ \mathrm{eV})$ observed in metalorganic vapor-phase epitaxy (MOVPE) GaP[13] have very different emission rates with respect to ours. The two levels due to oxygen in GaP $(\Delta E = 1.18$ and 1.08 eV$)$[9] seem to have emission rates nearest to the two levels observed in our study. However, our samples contain no intentional oxygen and any inadvertent oxygen would not be expected to be present in such high concentrations as observed in the present work. Besides, our preliminary optical work indicates that the photocapacitance signal from these levels has distinctly different charac-

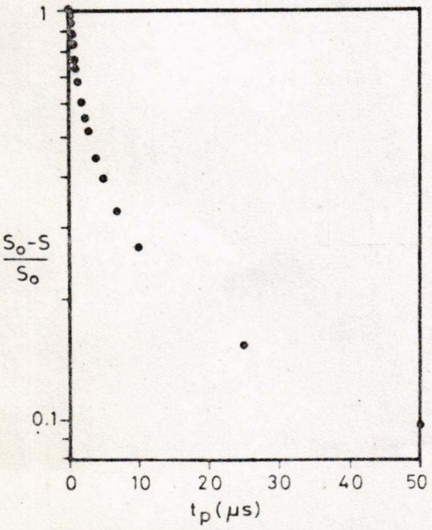

FIG. 4. Change in DLTS peak height S from its saturation value S_0 plotted against the DLTS excitation pulse width t_p. $V_R = -6$ V, $e_{\max} = 1.13\ \mathrm{s}^{-1}$, $T = 265$ K.

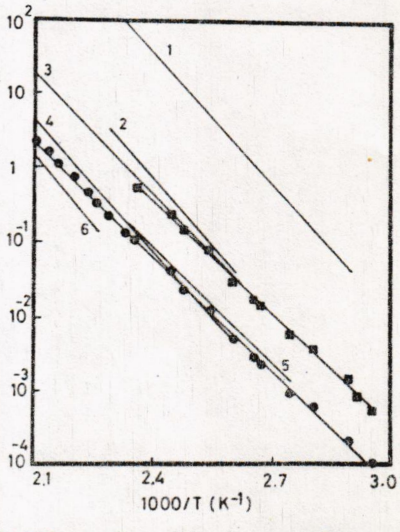

FIG. 5. Comparison of the electron emission rates (e_n) of the two levels observed in this work (squares and circles) with those of the previously reported mid-gap electron levels in GaP. 1 and 2 are levels D_5 and D_6 (Ref. 13), 3 and 4 are the two oxygen levels (Ref. 10), 5 is Cr-related level (Ref. 14), and 6 is $P_{Ga}^{+\,+}$ (Ref. 15).

teristics as compared to that obtained from oxygen. Thus, we are led to the conclusion that the two levels under discussion are not the well-known oxygen levels. The emission rates of a Cr-related level[14] ($\Delta E = 1.0$ eV) are somewhat larger but not very different from the deeper of the two levels reported in this work. However, it is unlikely that inadvertent Cr could be found in such large concentrations in LPE material. Brunwin *et al.*[14] found this level in concentrations of $\sim 10^{13}$–10^{14} cm^{-3} to be present inadvertently in VPE material but not at all in LPE material.

This leaves P_{Ga}^{++} as the possible candidate. This antisite defect ($\Delta E = 1.1 \pm 0.1$ eV)[15] has emission rates somewhat smaller than the measured values for the deeper of the two levels observed by us, but this discrepancy between the two sets of results might not be significant in view of the admitted limitations to the accuracy of the data of Ref. 15. However, there is one problem with this identification. If P_{Ga}^{++} were present in our samples in such large concentrations, one would expect P_{Ga}^{+} also to be present in similar concentrations. The only work reporting the energy position of the level due to P_{Ga}^{+} is that of Ferenczi *et al.*[15] who attribute a level 0.7 eV below the conduction band to P_{Ga}^{+}. In our samples, we have not found any level with significant concentration at such energies.

Thus, it would seem that the two levels observed in the present investigation are different from any midgap level in GaP reported in the literature to date. In view of the energy position of the two levels observed in this study, it could be speculated that one of these is the counterpart of the EL2 level in GaP. The speculation is particularly tempting in view of the fact that the energies of these deep levels agree well with the expected energy of the counterpart of EL2 in GaP extrapolated from the variation of EL2 energy with alloy composition in the $GaAs_{1-x}P_x$ alloy system.[4] This possibility is further strengthened because these levels are caused by some unintentional centers present in relatively large concentration and are, therefore, unlikely to be related to the presence of contaminant chemical impurities. In addition, it may be pointed out that a complex of the P_{Ga} antisite (PP_4) with an unknown entity (Y) replacing one of the four ligand phosphorus atoms—PP_3Y defect—has been reported to be associated with a near-mid-gap level in recent ODMR studies.[16] The energy position obtained from this work is roughly 0.8 ± 0.1 eV. Since these methods are known to provide rather uncertain energy estimates, one of the two levels observed by us could originate from the PP_3Y defect level. In view of the fact that, according to the present consensus an antisite-related center may be responsible for the EL2 defect in GaAs, it would appear that one of the two levels characterized in the present work may be the counterpart of EL2 in GaP.

V. CONCLUSION

In conclusion, we have performed detailed electron emission and capture measurements on two midgap levels in GaP, which could not be resolved in the preliminary TSCAP measurements reported by us earlier.[5] The activation energy for electron emission to conduction band from one level is found to vary from 0.88 ± 0.02 to 0.93 ± 0.02 eV from sample to sample, while for the other it is 0.96 ± 0.02 eV. A detailed comparison with the previously published emission rate data on midgap levels in GaP indicates that these levels had not been reported previously. It is suggested that one of the two levels may be a candidate for the counterpart in GaP of the well-known EL2 level found in GaAs. Furthermore, in view of the midgap nature of these levels and the fact that these are the dominant levels in our green-emitting LEDs, it is possible that these are the elusive 'killers' of luminescence efficiency of such LEDs.

ACKNOWLEDGMENT

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APPENDIX V

FIELD DEPENDENCE OF THERMAL EMISSION FROM OXYGEN IN GaP

Umar S. Qurashi, M. Zafar Iqbal and N. Baber
Semiconductor Physics Laboratory
Department of Physics
Quaid-i-Azam University
Islamabad, Pakistan

ABSTRACT

Deep level transient spectroscopy (DLTS) measurements of the field-dependence of thermal emission from a minority carrier deep-level in GaP, believed to be due to Oxygen, is reported here for the first time. A strong variation of the emission rate and the activation energy is observed, seemingly calling for a reappraisal of the existing model of the Oxygen defect due to Henry and Lang.

INTRODUCTION

Study of the electric field-dependence of thermal emission of carriers from a deep level is essential to provide a complete and unequivocal characterization of the associated defect centre. At the same time the field dependence data have often helped in modelling the potential-well associated with the centre and the mechanism of carrier emission from this well. A number of examples can be quoted - such as the Gold acceptor and the A-centre in Si [1] and Cr and EL2 in GaAs [2,3], which are all known to show strong field effects. This paper aims to present evidence for a similarly strong field dependence for emission from an important deep level in GaP.

MATERIAL AND SAMPLES

The material used in this study is liquid-phase-epitaxial (LPE) GaP deliberately doped with oxygen. The samples used are p-n junctions fabricated by double liquid phase epitaxy, manufactured as the standard red light emitting diodes (LED) by Ferranti Ltd., U.K. The n-side is doped with Te and p-side with Zn to about 10^{17} cm^{-3}. Oxygen is added to the p-layer during growth to produce red emitting Zn-O complex centres. The junctions are generally found to be linearly-graded type from the capacitance- voltage (C-V) analysis. The diodes, about 0.5mm x 0.5mm in size, were epoxy encapsulated after providing suitable ohmic contact leads.

EXPERIMENTAL DETAILS

The measurement of the field dependence of emission rates was carried out using a variation of the DLTS technique, employing a deep level spectrometer DLS-81, based on the lock-in principle [4], manufactured by Metrimpex, Hungary. The technique used, consisted of applying a double pulse sequence comprising of an injection pulse immediately followed by a majority carrier (zero volt) `clear´ pulse, as first proposed by Lang [5]. In order to ensure maximum filling of the minority carrier level we wished to study, a strong injection level was used. The signal, thus, came from a slice of the space-charge region extending from the metallurgical junction to the edge of the zero-bias depletion region. The applied field during emission was varied by changing the quiescent reverse bias from run to run. The detailed field dependence data for emission rates at different temperatures were obtained in one of two ways - (a) varying the reverse bias and hence the field while keeping the emission rate constant from one temperature scan to the next and subsequently repeating the whole set of measurements with different fixed emission rate windows, or (b) varying the emission rate while keeping the reverse bias fixed, resulting in the more familiar Arrhenius plots of emission rate versus inverse temperature. We found the data obtained by the two methods to be closely similar for a number of samples used in our study.

The magnitude of the average electric field in the active slice of the space-charge region at the temperature of emission, was obtained from a series of capacitance versus temperature measurements at the reverse bias values used for DLTS measurements and then applying the standard C-V analysis. The temperature dependence of the built-in voltage was measured and explicitly taken into account for the calculation of the field.

RESULTS AND DISCUSSION

A prominent minority carrier emission peak has always been observed in our DLTS spectra on red-emitting LEDs above room temperature. This is the dominant DLTS signal seen in any scan on these diodes. The lower limit on the concentration of the deep level corresponding to this peak is found to be ~ 3.0×10^{14} cm^{-3}. A small change in the applied reverse bias is found to shift the peak in a pronounced manner, pointing to a marked field-dependence of the emission rate. Typical emission rate versus field data are plotted in figure 1. for various temperatures ranging from ~ 350 K to ~ 480 K as permitted by the maximum allowed variation of the applied reverse voltage. The emission rate can be seen to rise roughly exponentially over this range of fields, for most temperatures. The T^2-corrected Arrhenius plots for various fields show a continuous but distinct variation of the slope with electric field, indicating a wide variation of the apparent activation energy - from ~ 0.5 eV to ~ 1.0 eV as the field decreases from ~ 7×10^5 V/cm to ~ 3×10^5 V/cm as shown in figure 2.

As the minority carrier peak under study represents the dominant deep-level signal from our samples which are deliberately doped with only one deep-level species, namely Oxygen on the p-side, it appears natural to presume that the minority carrier signal represents the emission of electrons captured by the Oxygen centres during the minority carrier injection pulse. Isolated Oxygen atoms substituting at phosphorous sites in GaP are known to act as double donors with a complex electronic structure, giving rise to two deep level states O_1 and O_2 [6]. Kukimoto etal [6] demonstrated a large lattice relaxation to be associated with the capture of the second electron. The electron and hole capture cross-sections reported by Henry and Lang [7] clearly indicate that only the state O_1 would be observable as the minority carrier (electron) emission centre in p-type GaP, as indeed was confirmed by their emission experiments which were conducted at low junction fields. Under low field conditions our measured emission rates and the apparent activation energy tend to agree with their values, which provides further support to our interpretation of the observed peak as the O_1 peak. However, it is for the first time

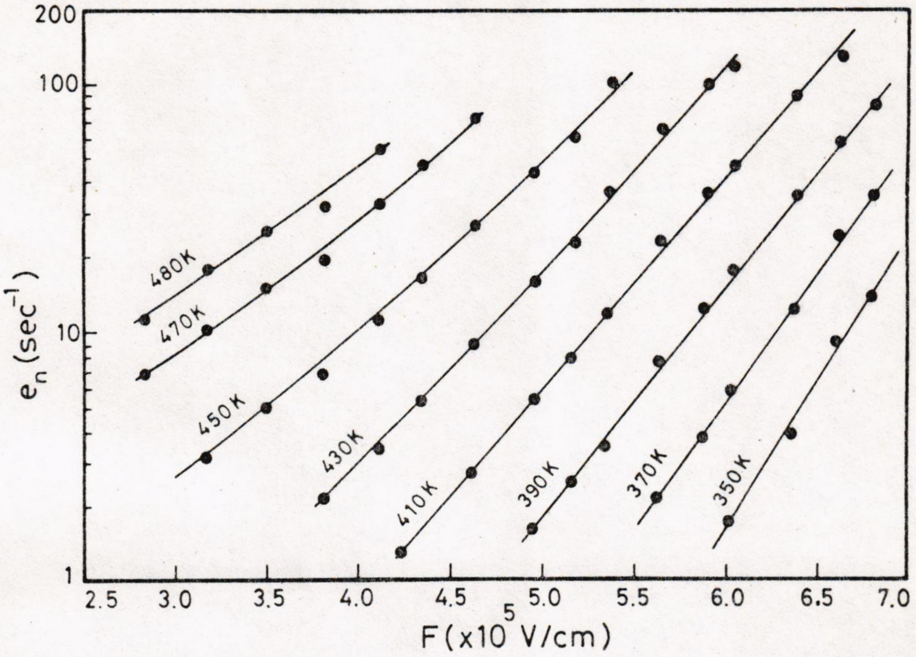

Fig.1. Measured variation of the emission rate (e_n) with electric field (F) at different temperatures.

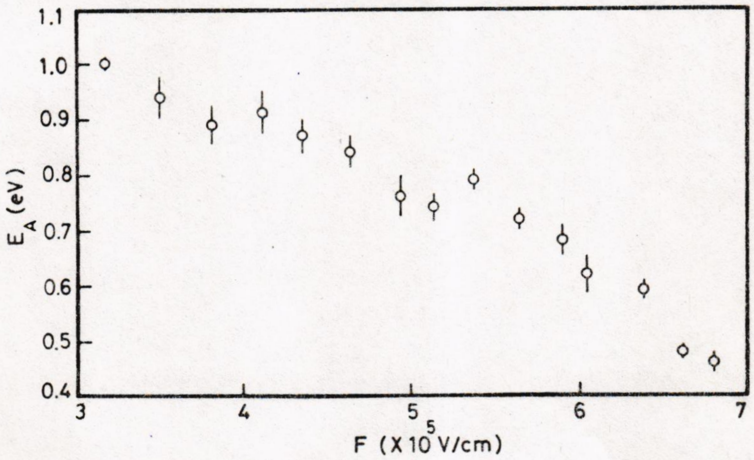

Fig.2. Variation of the thermal activation energy (E_A) with electric field (F).

that a strong field-dependence of electron emission from the O_1 state is being reported. Although both Kukimoto etal [6] and Henry and Lang [7] make a passing reference to the possibility of the emission from Oxygen in GaP being field dependent, neither of the two works has attempted to explicitly confirm and measure this field dependence. It is, however, significant to note that the activation energies given in these two reports are widely different, which would appear to be natural in the light of our finding. It is clear that the strong variation in the activation energy observed by us should necessitate a change in the various parameters involved in the construction of the large-lattice-relaxation configuration coordinate model of Henry and Lang [7] for the Oxygen defect.

CONCLUSIONS:

Electron emission from a dominant deep level in LPE GaP, attributed to Oxygen, has been demonstrated to be strongly field dependent, for the first time. This observation is expected to have strong implications for the established model of Henry and Lang for the Oxygen defect. Further work is needed to test all these implications and to understand the mechanism of field-dependent emission. Such work is in progress and will be reported elsewhere.

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APPENDIX VI

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Running Title:

Rôle of the mid-gap level as the dominant recombination center in platinum-doped silicon

Asghar A. Gill, N. Baber, and M. Zafar Iqbal
Semiconductor Physics Laboratory, Department of Physics, Quaid-i-Azam University, Islamabad, Pakistan

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The problem of identification of the dominant recombination center in platinum-doped silicon is investigated using deep-level transient spectroscopy (DLTS). Measurements using electrical and optical injection on platinum-doped *n* type silicon are reported. Results of measurements show that the recently observed platinum-related midgap level is an efficient recombination center and is probably responsible for the role of platinum as a lifetime killer. In addition, information is provided on the relative magnitudes of the electron and hole capture cross sections of the hitherto well-known deep levels assigned to platinum.

Deep-level impurities, such as gold, are commonly used to achieve fast switching speeds in silicon devices. Among the substitutes for gold as lifetime killer, platinum is probably the most prominent example which has received considerable attention in the literature. While in the case of gold impurity in Si it is clear that the midgap acceptor level is responsible for the recombination process, for platinum no such clear-cut choice of a level can be made from the numerous energy levels that have been reported to be observed in Pt doped Si (Ref. 1 and the references cited therein). It has been suggested[2,3] that the dominant recombination level of platinum lies at 0.42 eV above the valance band edge. However, this level has not been observed in many investigations of Pt-doped Si.[1,4,5] It is generally accepted that doping with platinum results in two deep levels with activation energies around $E_C - E_t = 0.23$ eV and $E_T - E_V = 0.32$ eV which are always present in Si:Pt as reported by various workers. The problem is that these two levels are not deep enough to explain the short lifetimes associated with silicon devices doped with platinum.[2] Besides, these two levels cannot explain the compensation effects reported by Jagadesh Kumar *et al.*[3]

Recently a mid-gap level has been observed[4,5,6] in *n*-type Si doped with platinum with activation energy for electron emission varying from 0.50 to 0.52 eV. Kwon, Ishikawa, and Kuwano[5] have carried out detailed concentration profiling on this level in Pt-diffused samples of Si and have found the profile to be M shaped with concentration falling down substantially near the surface. They have suggested this level to be platinum related and its low concentration near the surface to be the probable reason why earlier workers did not detect it. Because of its midgap nature, the level under discussion would be a very good candidate for the dominant recombination center in Si:Pt.

According to the theories of Shockley and Read[7] and Hall[8] the recombination rate depends exponentially upon the energy depth of a level from the band-gap edges and is, therefore, an important factor in determining the overall lifetime. However, for a level to be an efficient recombination center its electron and hole capture cross sections also have to be large. The electron capture cross sections for the platinum-related mid-gap level under discussion have been reported to be 1×10^{-14} cm^2 by Stoffler and Weber[4] and 4.5×10^{-15} cm^2 by Kwon, Ishikawa, and Kuwano[5] which are reasonably large. But the rate-limiting cross section is the minority-carrier cross section and no information about the hole capture cross section for this level is found in the literature.

In this communication we report results showing conclusively that the hole capture cross section of this midgap level is considerably larger than the electron capture cross section and hence, it is proposed that this is the lifetime controlling recombination level in Si:Pt.

Following the conclusion of Kwon, Ishikawa, and Kuwano[5] that the concentration of the Pt-related midgap level is low near the sample surface, diodes prepared on *n*-type material with low free electron concentrations (1.5×10^{14} cm^{-3}) were especially chosen for Pt diffusion to enhance the capacitance transient signal from the deep levels. These were prefabricated p^+ n junction diodes of Si manufactured by Rifa AB (Sweden). The n-type material was intrinsic LPE silicon and the p^+ layer was obtained by boron implantation. Platinum was sputtered on the back (n side) of the diodes and diffused at 850 °C for 2 h in sealed quartz ampoules in argon atmosphere. To avoid out-diffusion of platinum during cooling (a possible reason for the M-shaped profile of the level under investigation) the ampoules were rapidly guenched in water or oil. Platinum was later removed from the back surface by lapping and the diodes were mounted on T0-5 headers after providing Ohmic contacts of Ga rubbed with Al. The capacitance voltage (C-V) measurements performed after platinum diffusion showed the doping concentration on the n side to be $\simeq 1.4 \times 10^{14}$ cm^{-3}. Reference samples were also prepared that ~~which~~ underwent the same heat treatment without platinum deposition.

The measurements were performed using deep-level transient spectroscopy (DLTS).[9] The standard DLTS measurements were carried out using a Metrimpex (Hungary) Semitrap DLS-81 detection system based on lock-in principle. The optical DLTS was performed using a computer-controlled 17D060 system manufactured by SPC Electronics (Japan).

Figure 1 shows typical DLTS spectra observed by us. Curve (a) is obtained by applying reduced reverse bias pulses to the sample showing the majority-carrier (electron) emission spectrum. The peak (A) is due to the established $E_c - 0.23$ eV platinum level.[1] A high-temperature peak [marked (M) in figure] is clearly observed in all the spectra and corresponds to the midgap level of platinum since the reference samples do not show any of the DLTS peaks reported in this communication. Figure 2 gives the Arrhenius plot of emission rates from this level obtained from DLTS measurements. The activation energy obtained from this plot is $E_c - 0.55$ eV. The emission rate signature obtained from this plot agrees with the only other published emission rate data[6] for the midgap level in Si:Pt.

Curve (b) in Fig. 1 is obtained when forward bias pulses are applied to the sample, keeping other parameters the same as for the curve (a). The peak (A) corresponding to the $E_c - 0.23$ eV level is seen to reduce in magnitude while another minority-carrier emission peak (B) appears at 172 K. This is due to the other well-known platinum level with activation energy $E_v + 0.32$ eV.[1] The most striking feature of the curve (b) is that the peak (M) due to the 0.55-eV level disappears completely. This curve is taken for relatively high injection levels. For lower injection levels one finds this peak to be present but reduced in magnitude.

To further investigate the results of Fig. 1, we performed optical DLTS measurements on our samples for which the usual DLTS functions were carried out, except that optical pulses were used for carrier injection instead of electrical pulses. The sample was continuously kept at reverse bias while optical radiation of energy $h\nu$ higher than the band-gap energy of the semiconductor was made incident for the same durations for which electrical pulses were applied for the usual DLTS measurements. We used an 840-nm wavelength laser diode as the source of light. The above band-gap light produced electron-hole pairs that were captured by the deep levels and subsequently emitted thermally to give the DLTS spectrum. Figure 3 shows the results of optical DLTS. Curve (a) is the usual reduced reverse-bias DLTS scan similar to the one of curve (a) of Fig. 1. Curve (b) of Fig. 3 is the optical DLTS scan. Comparing with the curve (b) of Fig. 1, it is clear that while the main feature of disappearance of the peak (M) is retained, the effect on the other two levels is much more pronounced in Fig. 3. The peak A has been reduced very substantially while the peak B is much more pronounced in Fig. 3.

In n-type material, the DLTS peak height depends upon $\sigma_n n$ when no hole injection is involved. However, when holes are injected along with electrons the peak height might reduce, if $\sigma_p p$ is comparable to $\sigma_n n$, due to the competing process of hole capture. In the case of optical DLTS described above, $n \simeq p$ during capture (because the diode is kept under reverse bias when it is illuminated). Thus, the complete disappearance of the peak (M) in curve (b) of Fig. 3 implies that $\sigma_p > \sigma_n$ for the midgap level.

In electrical injection $p < n$, the exact value of p depending upon the level of injection. Comparing Figs. 1 and 3 it is inferred that in the case of Fig. 1 the injection level is lower than that of Fig. 3 since the effects of injection on peaks (A) and (B) are less pronounced in Fig. 1. Yet the peak (M) disappears even under these low-level injection conditions. This would imply that the difference in σ_p and σ_n is large for the midgap level. Accurate quantitative measurement of σ_p from our samples is not straightforward in view of the uncertainties and approximations involved in ascertaining the exact magnitude of hole concentrations p during injection. While these efforts are in progress, the results reported above demonstrate for the first time that for the platinum-related mid-gap level, $\sigma_p \gg \sigma_n$. This is obviously a result of significant importance for the understanding of the role of platinum as a recombination center and the identification of the midgap level as the efficient lifetime killer.

Applying the same criteria to the other two peaks in Figs. 1 and 3, it would appear that for the $E_c - 0.23$ eV level, σ_n is comparable but larger than while for the $E_v + 0.32$ eV level $\sigma_p > \sigma_n$. It must be emphasized that these conclusions might not be valid if these two levels are coupled. Brotherton and Bradley[10] have, however, presented some evidence to suggest that these two levels are not different charge states of the same center, in which case our conclusion would be valid. The only other reported values of both the cross sections for these two levels are by Brotherton and Bradley.[10] However, it is not possible to compare our results with their values since their two methods give vastly different values for the different cross sections and some of these are still different from those obtained from their earlier investigations.[1]

In conclusion, DLTS measurements on Pt-diffused p^+n Si diodes revealed the presence of three levels in all diodes: the well-known platinum levels with positions $E_C - 0.23$ eV and $E_V + 0.32$ eV in the band-gap and the midgap level (at $E_C - 0.55$ eV) which has been observed to be platinum related in relatively recent works. Minority-carrier injection and optical DLTS measurements revealed that for the midgap level $\sigma_p \gg \sigma_n$. Considering the near midgap nature of the $E_C - 0.55$ eV level and the previously reported large σ_n for it, the additional information, i.e., $\sigma_p \gg \sigma_n$, provided by the present work clearly leads us to propose that this level is the dominant recombination center in Si:Pt.

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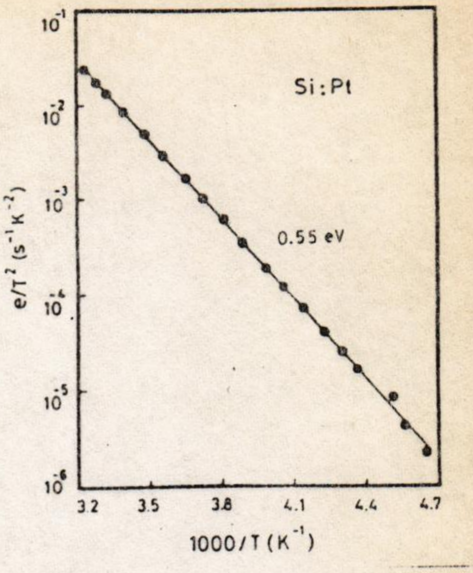

FIG. 2. The electron emission rate data for the platinum related midgap level.

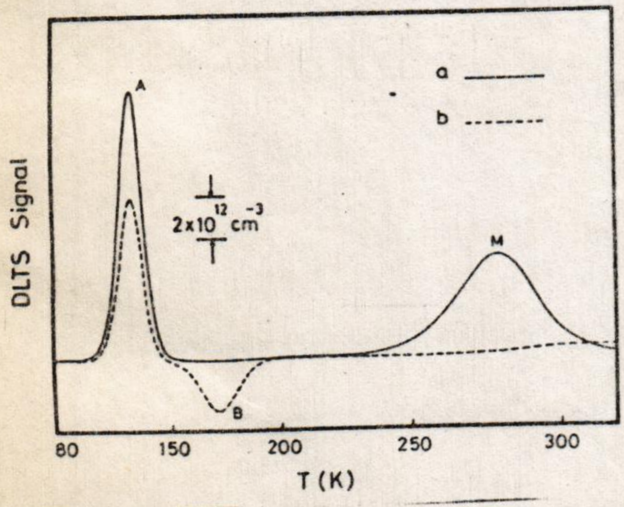

FIG. 1. DLTS spectra of a platinum-doped p^+n Si diode, $V_R = -4$ V, $e_{max} = 228.8\ s^{-1}$; (a) (full curve): reduced reverse-bias spectrum, (b) (dashed curve): electrical injection spectrum.

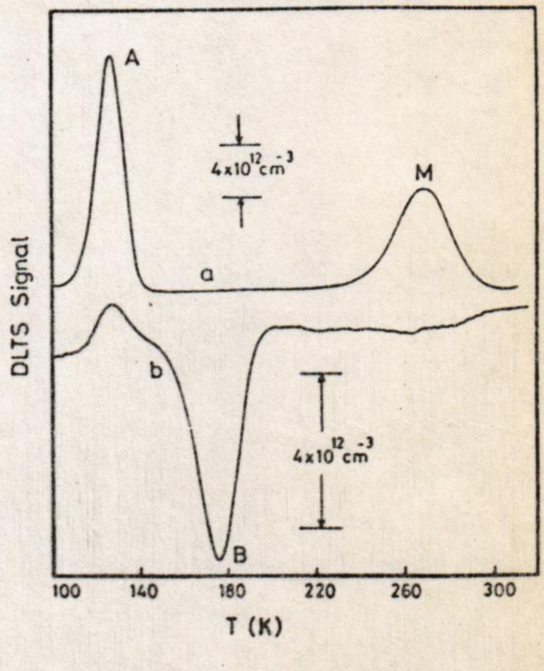

FIG. 3. Optical DLTS results of the diode of Fig. 1. Curve (a) is the reduced reverse-bias spectrum while curve (b) is the optical DLTS spectrum. $V_R = -4$ V, $e_{max} = 60.8\ s^{-1}$.