Electric-field dependence of electron emission from the deep-level oxygen defect in GaP

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Deep-level transient spectroscopy (DLTS) is shown to reveal a strong field dependence of the thermal emission of electrons from the singly occupied state (O_1) of the deep-level oxygen defect in GaP. Detailed data on this field dependence and its variation with temperature over the range 350–470 K are reported. The experimental results are analyzed in terms of the phonon-assisted tunneling model of Makram-Ebeid and Lannoo. Good agreement is found between experiment and theory for the entire range of measurements. The values for physical parameters, such as the Franck-Condon shift, obtained from this fit are compared with published results from luminescence spectroscopy and other techniques on oxygen and other defects in GaP. Our study suggests a reappraisal of the configuration-coordinate model of oxygen in GaP proposed by Henry and Lang.

I. INTRODUCTION

Oxygen in GaP is one of the most well-studied deep-level impurities in semiconductors.[1] Its technological importance in being associated with the recombination center responsible for red light emission (the Zn-O complex) was the prime motive behind the initial studies. Later studies, however, turned out to be extremely rewarding insofar as they yielded rich data unveiling intriguing aspects of the fundamental physics of defects in semiconductors. The results of these studies generated controversies regarding the nature of the oxygen defect center and particularly its electronic structure, some of which persist[2] in spite of nearly three decades of work on GaP:O. In brief, oxygen which normally substitutes for phosphorus in GaP has been shown to act as a donor having two deep-level states in the band gap corresponding to the three charge states, viz. neutral, positive, and negative. Detailed configuration-coordinate diagrams, based on the largest lattice relaxation induced by electron occupation yet discovered in semiconductors until then, have been given by Henry and Lang[3] after pooling down thermal and optical data from the junction space-charge and luminescence spectroscopy techniques, for both deep-level states of oxygen. The lattice relaxation following the capture of the second electron causing an energy-level shift of ~ 1.56 eV (Ref. 3) is so huge that many researchers doubted this large-lattice-relaxation model, thus leading to some controversy. One important parameter used in constructing these configuration-coordinate diagrams is the thermal activation energy of the electron into the conduction band from the respective deep-level states. This energy is usually obtained from an Arrhenius analysis of the emission rate data acquired by using junction space-charge transient techniques such as single-shot capacitance transients or deep-level transient spectroscopy (DLTS) technique.[4] One problem with these junction space-charge transient techniques is, however, that they measure the thermal emission rates in the presence of the high built-in junction field which is known to significantly affect the activation energy of many, though not all, deep-level centers.[5] It is clear, therefore, that the validity and accuracy of any model of the electronic structure of a deep-level defect center such as oxygen in GaP will depend crucially on a careful measurement of the field dependence, if any, of the carrier emission rates. The important Zn-O complex in GaP is a classic example where the significant field dependence of the emission rate did, indeed, seriously modify the understanding of the configuration-coordinate diagram and the recombination kinetics of this center.[2]

No such serious effort has been made to obtain detailed field-dependence data for the emission from the O centers in GaP in spite of all the important debates on this system. Interestingly though, two very different sets of values for the activation energies of the two oxygen states O_1 (one-electron) and O_2 (two-electron), namely 0.78 eV and 0.76 eV from the earlier work[6] and 1.18 eV and 1.08 eV, respectively, from the later work[4] of the same research group have been reported in the literature. The remark by Henry and Lang[3] that field dependence of the emission rates *may be* the possible cause of this discrepancy is the only available passing reference to this effect in the case of oxygen deep centers by Henry and Lang.[3] A detailed quantitative investigation of this aspect of oxygen in GaP is, therefore, called for and is the subject of this paper. Results of our preliminary investigations already provided evidence for a strongly field-dependent emission from oxygen.[7] Detailed further measurements of the field-dependent electron emission from the oxygen defect and the theoretical analysis of these data are reported here.

II. MATERIAL AND SAMPLES

The material used in this study is liquid-phase-epitaxial 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., United Kingdom. The *n*-type side is doped with Te and *p*-type side with Zn to about 10^{17} cm^{-3}. Oxygen is added to the *p*-type layer during growth to produce red-emitting Zn-O complex centers. The junctions are generally found to be linearly graded type from the capacitance-voltage (*C-V*) analysis. The diodes, about 0.5 mm$\times$0.5 mm in size, were epoxy encapsulated after providing suitable Ohmic contact leads.

III. MEASUREMENTS

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,[8] manufactured by Metrimpex, Hungary. The technique used consisted of applying a double-pulse sequence comprised of an injection pulse immediately followed by a majority carrier (0 V) clear pulse, as first proposed by Lang.[4] 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. It is obvious that unlike the case of emission from majority-carrier levels,[9] we cannot decrease the width of the depletion region slice and hence the spread in the field value to as narrow a region as we would like. 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.

IV. RESULTS

The DLTS spectra of our samples obtained by using minority-carrier injection pulses always show a dominant peak above room temperature as seen in Fig. 1. This peak is found to shift markedly to lower temperatures as

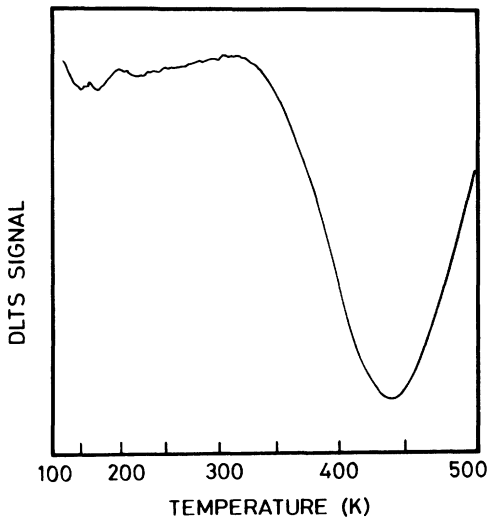

FIG. 1. Single-pulse injection DLTS scan on a GaP red LED showing the dominant oxygen (O_1) peak; emission rate equal to 9.04 sec^{-1}; reverse bias equal to 10 V.

the applied reverse bias for DLTS is increased slightly as is clear from Fig. 2. This is clear evidence for field-dependent emission of minority carriers from the corresponding deep level. While the exact concentration of this level cannot be obtained because of the usual uncertainties involved in determining the injected minority-carrier density, a lower limit can be easily obtained from the observed peak height. The defect concentration responsible for this deep level is thus typically found to have a minimum value of $\sim 3.0\times10^{14}$ cm^{-3} in our samples.

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*-type side, it appears natural to presume that the minority-carrier signal represents the

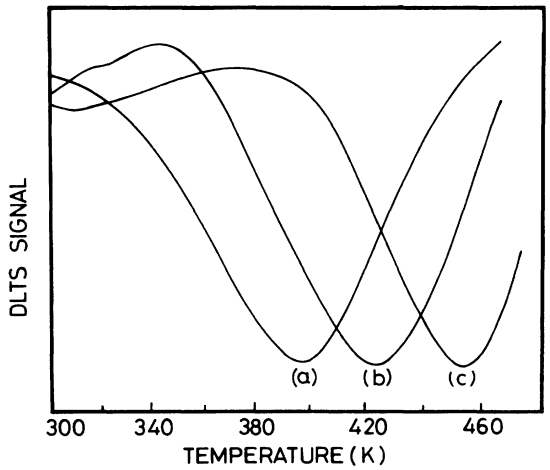

FIG. 2. Double-pulse DLTS scans showing the shift in peak position as the field F is changed. The emission rate is equal to 8.97 sec^{-1}; (a) $F=5.3\times10^5$ V/cm; (b) $F=4.4\times10^5$ V/cm; (c) $F=3.4\times10^5$ V/cm. The base line has been shifted for better comparison of peak positions.

emission of electrons captured by the oxygen centers during the minority-carrier injection pulse. Isolated oxygen atoms substituting at phosphorus sites in GaP are known to act as donors with a complex electronic structure, giving rise to two deep-level states O_1 and O_2, as mentioned above. The electron and hole capture cross sections reported by Henry and Lang[3] clearly indicate that only the state O_1 would be observable as the minority-carrier (electron) emission center 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. Our identification is also consistent with the DLTS peak position observed by Henry and Dapkus[10] on their GaP LED's, considering the typical electric-field value for their devices.

The detailed field dependence of electron emission from the O_1 state was determined using the specific techniques outlined in Sec. III at a number of temperatures covering the range ~350–480 K, up to the maximum variation of the electric field permitted by the breakdown of the junction. The data showed the electron emission rate of O_1 to rise almost exponentially with the electric field as can be seen from Fig. 3. This field dependence is so strong that if interpreted in terms of a variation of the apparent thermal activation energy E_A, it leads to a variation in E_A from ~0.5 to ~1.0 eV as the field decreases from $\sim 7\times 10^5$ to 3×10^5 V/cm, as discussed earlier by us.[7]

A number of models of the field-enhanced emission have been proposed in the literature based on (a) the Poole-Frenkel mechanism, (b) tunneling through the barrier, and (c) a phonon-assisted tunneling mechanism, using various forms of potential wells[11] representing the defect. Clearly, such a strong field dependence as observed by us cannot be explained by the Poole-Frenkel effect. The pure tunneling mechanism, on the other hand, becomes operative only at very high fields ($\sim 10^7$ V/cm). The alternative mechanism which has been successfully invoked in an increasing number of cases[5] lately is the phonon-assisted tunneling. This can be viewed as the thermal analog of the optical Franz-Keldysh effect. Vincent, Chantre, and Bois[12] have developed a semiclassical theoretical expression on this basis for the field-enhanced emission rate from a Coulomb potential well and demonstrated its success in explaining their data for the Cr deep level in GaAs. Makram-Ebeid and Lannoo[13] later proposed a quantum theory of the phonon-assisted tunneling model and demonstrated an extremely good agreement between the theoretically predicted field dependence of the emission rate as well as the variation of this dependence with temperature and the experimental data for the important $EL2$ defect in GaAs.

We have tried to apply the Makram-Ebeid–Lannoo theory to analyze our data. Their theoretical expression for emission rate e_n as a function of electric field F is

$$e_n(F)=e_n(0)+\sum_{m=-M_0}^{0} W_m^c P(\Delta_T+m\hbar\omega) \tag{1}$$

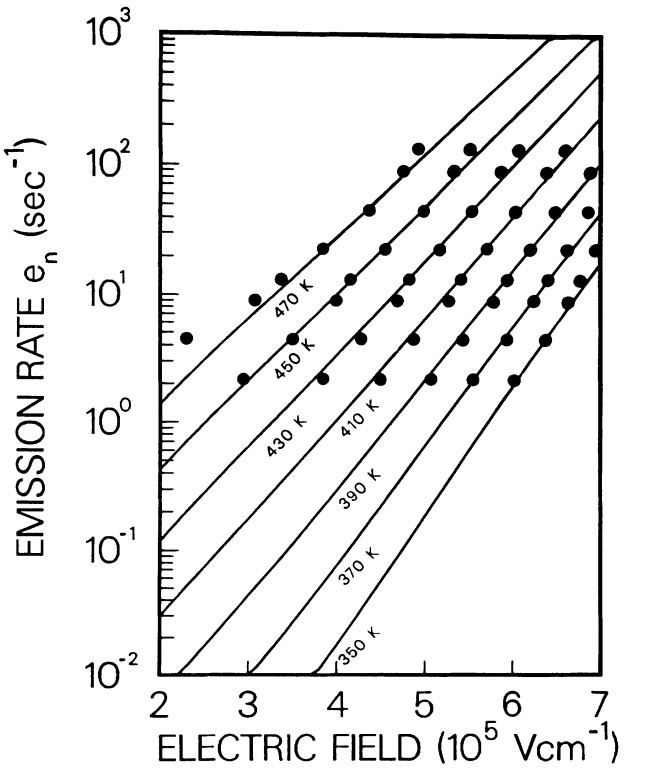

FIG. 3. Electric-field dependence of the electron emission from the oxygen level O_1 in GaP. Solid circles are the data points and lines represent the theoretical fits from the Makram-Ebeid–Lannoo model. The parameter values used for the theoretical fit are $S\hbar\omega=262$ meV, $\hbar\omega=36.54$ meV, $\Delta_T=950.27$ meV, $\gamma=12.38$, and $m^*=0.18m_e$.

with

$$M_0=\Delta_T/\hbar\omega\ , \tag{2}$$

$$W_m^c(S)=\exp\left[\frac{m\hbar\omega}{2kT}-S\coth\left[\frac{\hbar\omega}{2kT}\right]\right]\times I_m\left[\frac{S}{\sinh(\hbar\omega/2kT)}\right], \tag{3}$$

$$P(\Delta)=\gamma\Delta e^{-A}/A \equiv\gamma\frac{qF}{4\hbar}\left[\frac{\hbar^2}{2m^*\Delta}\right]^{1/2}\times\exp\left[-\frac{4}{3}\left[\frac{2m^*}{q^2\hbar^2}\right]^{1/2}\frac{\Delta^{3/2}}{F}\right]. \tag{4}$$

Here I_m is the modified Bessel function of order m, $e_n(0)$ and Δ_T are the zero-field values of the emission rate and the binding energy of the deep-level defect, respectively, m^* is the effective mass of the electron, k the Boltzmann constant, T the absolute temperature, and q the electronic charge. The theory requires fitting of three parameters: γ, which is essentially an adjustable fudge factor: S, the Huang-Rhys factor; and $\hbar\omega$, the characteristic energy of the phonons assisting the tunneling. $S\hbar\omega$ thus provides

information on the Franck-Condon shift of the deep-level defect.

A slight difficulty arises in applying the Makram-Ebeid–Lannoo theory to GaP since it assumes an isotropic conduction band, while the conduction-band minimum of GaP is highly anisotropic with the longitudinal and transverse effective masses $m_{\parallel}^{*}=1.5m_e$ and $m_{\perp}^{*}=0.18m_e$, where m_e is the free-electron mass.[14] On taking this anisotropy into account, we found that the lowest effective mass is the determining value. Our theoretical fits have, accordingly, been obtained with $m^{*}=0.18m_e$. The results of a best fit of our emission rate data for the oxygen level O_1 with the above expression are shown as solid lines in Fig. 3. The agreement between the Makram-Ebeid theory and our data can be seen to be very good for almost the entire range of temperatures. The values of the parameters used for these fits are

$$\Delta_T=950.27 \text{ meV},$$

$$\hbar\omega=36.54 \text{ meV},$$

$$S=7.17,$$

$$\gamma=12.38$$

for the particular sample used for the data plotted in Fig. 3. Best fits to data on other samples yield values very close to these. We have tried different values of the fitting parameters—in particular, the phonon energy $\hbar\omega$. Using a value of $\hbar\omega=20$ meV, close to that quoted for the Zn–O deep-level complex in GaP, for instance, we obtain a best fit for almost the same value of the Franck-Condon shift ($S\hbar\omega\simeq 262$ meV) as used for the fit shown in Fig. 3. This is understandable since our data are obtained at relatively high temperatures and S and $\hbar\omega$ appear only as the combination $S\hbar\omega$ in the high-temperature approximation to the theory.

V. DISCUSSION

Our field-dependence data interpreted in terms of the Makram-Ebeid–Lannoo model thus yield a Franck-Condon shift of ~ 262 meV with a zero-field thermal activation energy $\Delta_T\sim 0.95$ eV. This value of the Franck-Condon shift is significantly larger than the value of ~ 90 meV obtained by Henry and Lang[3] from the low-temperature luminescence data corresponding to capture and recombination at the O_1 donor and by Kopylov and Pikhtin[15] from their analysis of the phonon broadening of the hole photoionization cross section. The optical binding energy of the electron at this level has been shown by Henry and Lang[3] to be 0.96 eV after attributing a lattice-relaxation energy change of ~ 0.2 eV to the level position. Our value $\Delta_T+S\hbar\omega\simeq 1.2$ eV for the optical binding energy is evidently larger owing to a much higher Franck-Condon shift as compared to that estimated by Henry and Lang from a fitting of the luminescence data to their configuration-coordinate model. Our value of $S\hbar\omega$ is, however, not significantly different from the value of this parameter for the Zn-O center in GaP (190–206 meV) obtained from an analysis of field dependence of thermal emission similar to ours, by Makram-Ebeid[16] and from luminescence data on the same center by Henry and Lang.[3] This shows that such large values of $S\hbar\omega$ as inferred from our observed field dependence of emission from the O_1 level are not uncommon for deep levels in GaP. Whereas it should be borne in mind that our field-dependence data represent the average variation of emission rate from O_1, in view of the limitations of our measurements mentioned in Sec. III, the discrepancy between our value and that of Henry and Lang may, in our opinion, arise from the following causes.

(a) The luminescence data coupled with the intricacies of their configuration-coordinate model may inherently require a different value of $S\hbar\omega$ as compared to that required by the field dependence of thermal emission. In effect, the analysis of the optical data with the configuration-coordinate model can be oversimplified, for example, when the excited states correspond to degenerate states.[17] In consequence, one should reconsider the interpretation of the optical measurements such as luminescence in view of our new results.

(b) Henry and Lang[3] have carried out their analysis using luminescence data obtained at low temperatures, whereas our data are obtained at much higher temperatures (350–470 K). Factors such as the variation of the binding energy with temperature may lead to uncertainties in comparing the parameters.

VI. CONCLUSIONS

It is clear that the phonon-assisted tunneling model of thermal emission provides a good explanation of the field-enhanced electron emission data for the one-electron deep state O_1 attributed to oxygen in GaP. In particular, the Makram-Ebeid–Lannoo quantum theory has been shown to be in excellent agreement with our data over a wide range of temperatures. The values of the physical parameters such as the Franck-Condon shift inferred from the fit, though not in agreement with the previously reported values from low-temperature luminescence data are, however, not uncommon for deep levels in GaP. Measurements of the field dependence of electron emission for oxygen levels in n-type GaP doped with oxygen, allowing more precise field-dependence measurements using differential DLTS technique,[9] may provide an improved quantitative comparison with the theories. The clearly observed strong field dependence of the emission rate would, however, already warrant a modification in the lattice frequency change (ω_1 to ω_2) for the state O_1 on electron capture and hence in the configuration-coordinate model proposed by Henry and Lang,[3] because of the required reevaluation of the Franck-Condon shift and the optical binding energy.

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