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Study of the main electron trap in $Ga_{1-x}In_xAs$ alloys

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Transient-capacitance-spectroscopy experiments yielded electron-emission-rate and electron capture cross-section versus temperature data for the main electron trap in vapor-phase epitaxial $Ga_{1-x}In_xAs$ layers with $0 < x < 0.21$. The ionization energy E_C-E_T was obtained from these. Theoretical calculations using the pseudopotential method were performed for substitutional oxygen donor in GaInAs, and the calculated energy levels were compared with the experimental ones. The electron-capture cross sections, as well as optical photoionization data are also discussed from the theoretical point of view. It is argued that most of the experimental evidence is not consistent with the idea that the observed electron trap is simple (substitutional) donor oxygen.

I. INTRODUCTION

The deep levels may play an important role in the operation of specific semiconductor devices, particularly in optoelectronics. In recent years, largely due to improvements in the experimental techniques which tend to become more quantitative, and also due to the development of efficient tools for theoretical investigation, some progress has been made towards understanding the electronic and optical properties of these levels, their physicochemical origin, and the physical configuration of the corresponding defects.

Most of the recent studies deal with III-V semiconductors, in view of their applications in optoelectronics. A recent review of the situation in GaAs and GaP has been prepared by Ikoma and co-workers.[1]

Particle irradiation of semiconductors is a convenient means for creating defects (and therefore deep levels) in a controlled fashion. A recent review on irradiation defects in III-V semiconductors has been presented by Lang.[2] Equally important, but more difficult is the study of the defects which appear spontaneously in as-grown materials, since the means available for controlling the presence and concentration of these defects are limited. Since none of the deep levels corresponding to these "natural" defects have electronic properties identical with those of the defects created by irradiation, one may conclude that they are not simple lattice defects, e.g., anion or cation vacancies or interstitials; more likely, they are due to impurities and impurity-lattice defect complexes.

In the case of III-V semiconductors, one of the useful ways of investigation of the "natural" deep levels is to follow the variation of their properties as a function of composition in pseudoternary alloys. The first such tentatives have been accomplished by Lang[3] and Majerfeld[4] for the system $Ga_{1-x}Al_xAs$.

We present here a study of this type, concerning the system $Ga_{1-x}In_xAs$ and the deep level, already well known for GaAs, labeled electron trap "A" in our previous publications[5] or "O" in recent papers by Lang[6]; the last label points to the fact that this deep level may be due to oxygen, either in the simplest configuration of a substitutional atom on arsenic site, or in an impurity-lattice defect complex. An attempt to discover whether the level can be identified with the simple substitutional oxygen impurity has been one of the motivations of this study. In addition to the new experimental results which will be presented for the alloys, we have endeavored to compare the experimental results with detailed, specific theoretical calculations, hoping to establish a new tradition and make a step forward with respect to previous work. In Sec. II, we briefly discuss the existing evidence concerning the origin of electron trap A and its possible relation to oxygen. In Sec. III, we describe the techniques used in the experimental study, as well as the experimental results concerning the emission and capture rates for level A in GaInAs alloys of various compositions. Section IV deals with the theoretical calculations and their comparison with experiment. Section V is a summary.

II. REVIEW OF THE EXPERIMENTAL EVIDENCE ON DEEP LEVELS POSSIBLY RELATED TO OXYGEN IN GaAs

The deep electron trap which forms the object of the present study has been known for a long time and it seems to be by far the most common of the unintentionally created deep levels in GaAs, both

bulk grown and vapor-phase epitaxial (VPE). The level has been studied most often by two different techniques in two different types of material, namely, photoconductivity in high-resistivity samples and capacitance transients in p-n junctions, or Schottky barriers, in low-resistivity ones. For discussions of previous studies of the second kind we refer to Lang *et al.*[6] and Mircea *et al.*[5]

The tentative attribution of this level to oxygen is strongly supported by the investigation of the high-resistivity bulk-grown material, since the concentration of the level greatly increases when the material is deliberately doped with oxygen.[7-9] The photoionization spectral response data taken on such samples often reveal[7,9,30] two distinct contributions with threshold energies at 0.75–0.8 eV and around 1.05 eV. Grimmeiss *et al.*[9] have recently shown that the same thresholds are also observed in p^+n junctions on low-resistivity material and that they correspond to transitions from the deep levels into the conduction band.

The question then arises whether both these levels belong to the same defect center, more generally, whether they are both related in some way to the presence of oxygen in the semiconductor.

The concentrations of these deep levels in bulk-grown material are usually rather high, typically in the 10^{16}-cm^{-3} range, so that they are easily observed, but other levels are generally present as well in this kind of material,[7,10] which renders the interpretation more difficult. In this respect, the situation is clearer with epitaxial material. From our previous photoconductivity and transient capacitance experience with VPE, GaAs[11,12] and its comparison with deep level transient spectroscopy (DLTS) work by Lang and Logan,[6] photocapacitance work by Bois and Boulou,[13] photocapacitance and transient-capacitance work by Sakai and Ikoma,[14] as well as with Grimmeiss and Ledebo,[9] and Lin *et al.*,[30] we draw the following conclusions: (i) the two levels referred to above are also present in undoped VPE material, although at much lower concentrations, typically 10^{13}–10^{14} cm^{-3}; (ii) the two levels are independent from one another. The level with photoionization threshold at 1–1.05 eV from E_c (and 0.42–0.45 eV from E_v) is directly related to copper.[6,12] Therefore, the hypothesis of a double level (a defect with two ionization states) proposed by Bois[13,15] is not verified. However, it is shown in Sec. III B 2 below that the "A" electron trap, which is the level with photoionization threshold at 0.75–0.8 eV, seems to have at least one of the features which are characteristic for a defect with two ionization states.

As further evidence for the fact that the "oxygen" level in bulk-grown GaAs is indeed the same as

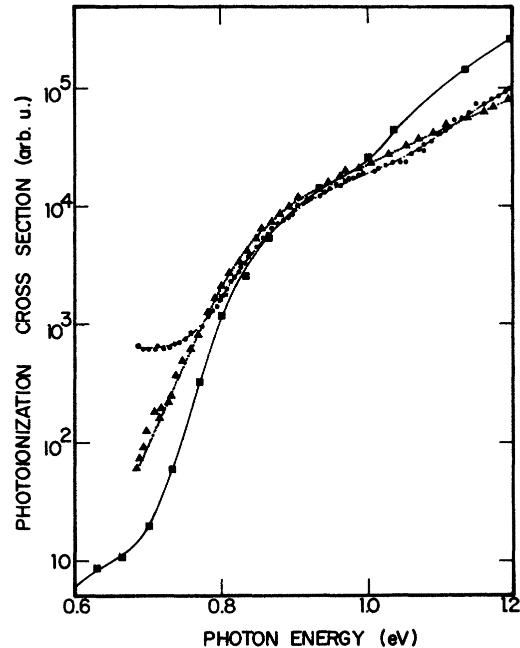

FIG. 1. Extrinsic photoconductivity in GaAs at 100 K. Triangles—high-resistivity oxygen-doped bulk (Ref. 9); crosses and circles—two different low-resistivity (1 Ω cm) VPE layers with the substrate etched off (Ref. 11).

"A" electron trap in high-purity VPE material, we present in Fig. 1 photoconductivity spectra measured on thin (10^{-2} mm) epilayers with the substrate removed.[11] The two photoionization curves for two different epilayers are essentially identical in the range 0.75–1.0 eV and are in agreement with the recent data for oxygen-doped bulk. The threshold at 1–1.05 eV is strong only in one of the two epilayers, in agreement with statement (ii) above.

III. EXPERIMENTAL STUDY OF THE A ELECTRON TRAP

A. Preparation of semiconductor material and samples

The material was prepared at *Laboratories d'Electronique et de Physique applique (LEP)* by vapor phase expitaxial growth using the $AsCl_3$ process under hydrogen flow. The substrates were n^+ doped and oriented 3° off (100). The source and substrate temperatures were 800 and 720 °C, respectively. Growth rate was 10 μm/h. In order to reduce the effects of lattice mismatch, the In content was increased in steps.[16] The dislocation density in the final, constant composition layer was in the 10^5-cm^{-2} range.

The epilayers were visually examined, then their composition was determined by using the x-ray measurement of the lattice parameter. The band

gap was estimated from the infrared absorption threshold at room temperature in the so-called "water-droplet" experiment,[17] this measurement being subsequently used as a routine check of alloy composition. Preliminary electrical characterization included conductivity type and free-carrier-concentration profile determinations using a mercury Schottky barrier.

Without intentional doping, the layers were n type with electron concentrations of $10^{15}-10^{16}$ cm^{-3}. For our study, low electron concentrations are highly desirable, in order to be able to measure the electron-capture rates (see Sec. III B 2 below); however, for compositions with large indium content it has not been possible to obtain low doping levels. On the layers chosen for transient-capacitance experiments, the doping profile measurements were repeated, with better accuracy, on the permanent Schottky barriers used in these experiments.

The barriers were circular gold plots with a diameter of 0.9 mm, obtained by vacuum evaporation through a nickel mask in an oil-free vacuum setup. No cleaning procedure was applied to the wafers prior to evaporation, but considerable care was taken to reduce surface pollution as much as possible. The Ohmic contact was made by soldering a tin ball on the edge of the sample. The connection to the barrier was realized with a gold wire fastened with silver paste. A more detailed description of the sample mounting has been given in a previous report.[18]

In Table I, we summarize the main characteristics of the samples chosen for this study. A range of indium content from (0–24)% has been explored. The samples listed in the table had fairly uniform electron concentration profiles.

TABLE I. Survey of $Ga_{1-x}In_xAs$ wafers used in this study.

Wafer n^0	x [a]	E_x [b] (eV)	n [c] (cm^{-3})	w [d] (μm)	N_t [e] (cm^{-3})
1	0.046	1.320	1.2×10^{16}	10	2×10^{13}
2	0.077	1.265	8×10^{14}	20	7×10^{13}
3	0.099	1.245	7.5×10^{15}	20	10^{14}
4	0.140	1.215	7×10^{15}	3	4×10^{13}
5	0.21	1.115	1.5×10^{16}	20	4×10^{13}
6	0.24	1.075	2×10^{16}	11	4×10^{13}
GaAs	0	1.37	2×10^{15}	20	2×10^{14}

[a] Composition as deduced from x-ray lattice parameter measurements.

[b] Band gap evaluated at room temperature from the spectral response of a water-droplet barrier on semiconductor.

[c] Free-carrier (electron) concentration at room temperature; accurate to within 20%.

[d] Thickness of the layer of GaInAs with uniform composition.

[e] Concentration of deep electron trap A calculated from the height of the DLTS peak.

B. Transient-capacitance experiments

We have measured the emission rates (from deep level to conduction band) and the capture rates (from conduction band to deep level) as a function of temperature.

1. Emission rates

We have mainly worked with the dynamic, differential measurement of capacitance transients introduced by Lang[19] under the name DLTS. Two different experimental systems were used. The first, semiautomatic system based on a Hewlett-Packard model 9821 calculator has been described previously[18]; it can measure from very small emission rates (starting at 10^{-3} s^{-1} or so) up to 10 s^{-1}. The second system, extending the range from about 10 s^{-1} to 5×10^3 s^{-1}, is an analog one and is based on the use of a network analyzer (HP model 8407 A), as capacitance meter with a signal of 0.1 V applied to the sample, and a lock-in detector (PAR model 128) as filter selecting the fundamental of the repetitive transient. This last setup, schematically shown in Fig. 2, is characterized by an excellent signal-to-noise ratio, due to the efficient use of information and in spite of the relatively high level of noise coming from the network analyzer.

In Fig. 3, we show the DLTS spectra, taken with

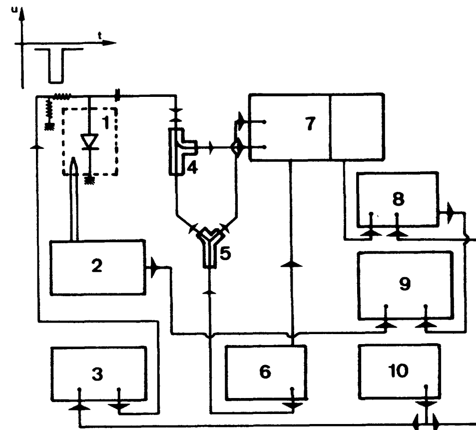

FIG. 2. Schematic drawing of the electronic setup for transient capacitance spectroscopy at moderately high emission rates. (1) Sample in cryostat, (2) digital thermometer CRL 204, (3) pulse generator HP 8015 A, (4) directional coupler HP 8721 A, (5) power splitter, (6) rf generator HP 8601 A, (7) network analyzer HP 8407 A with display 8412 A, (8) lock-in detector PAR 129, (9) x-y recorder, (10) square-wave generator.

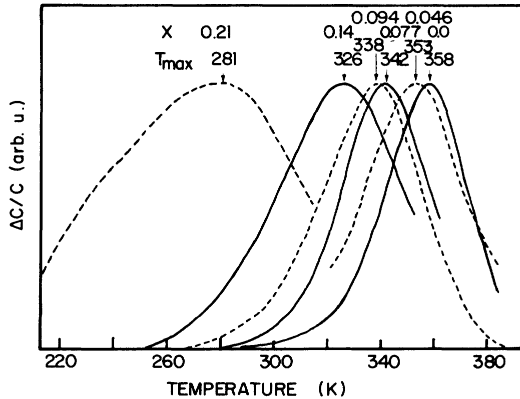

FIG. 3. DLTS spectra with a fixed-emission-rate window as a function of alloy composition. C is the capacitance of the barrier.

an emission-rate window centered at 7.5 s^{-1}: on samples made from pure GaAs and from alloys 1, 2, 3, and 4. For easier comparison, the spectra have been redrawn with normalized amplitudes, while in reality the peaks were of course unequal—the peak height being proportional to N_t/n, where N_t is the deep-level concentration. In the range of temperatures investigated (−190 to +160 °C), a single electron trap peak was observed for each sample. Also, the peak position monotonously moves toward lower temperatures as the indium fraction x increases, which is exactly what one expects if the same defect is responsible for the peaks observed in the different samples. From these observations, and taking into account that the layers were grown in the same reactor under similar conditions, we conclude with a high degree of credibility that the same defect is observed over the whole composition range.

The temperature T_{max} corresponding to the DLTS peaks of Fig. 3 are plotted as a function of indium

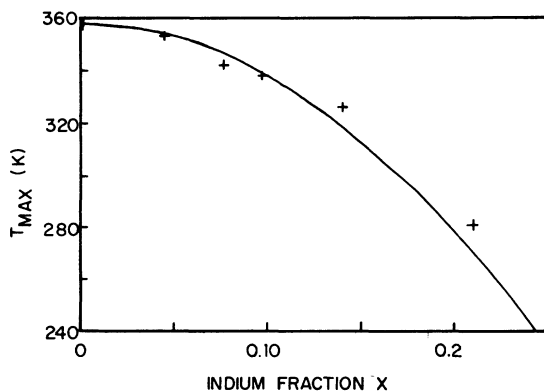

FIG. 4. Plot of temperatures T_{max} of Fig. 3, corresponding to an emission rate of 7.5 s^{-1} vs indium fraction x.

fraction x in Fig. 4. A parabolic law

$$T_{max} = T_{max}(0) - T_{max}(x) = ax^b$$

with $b = 2$, $a = 2000$ K, allows one to reproduce the experimental results quite faithfully; this *empirical* fit is also shown in Fig. 4. Still, nonsystematic differences, significantly larger than the experimental error, exist between the smooth fit and the data. These differences have probably to do with two "secondary effects" which we have observed:

(i) Even in the simplest case of the binary semiconductor GaAs ($x = 0$), the dependence of emission rate versus temperature $e_n(T)$ is not unique; it can slightly, but significantly vary from layer to layer, even if these are of a similar kind (VPE, doping in the 10^{15}-cm^{-3} range, relative trap concentration N_t/n much smaller than unity).

(ii) While, in the case of pure-GaAs samples, the emission transients are rigorously exponential, this is no more true for our alloy samples, in which more complex transients with several time constants are obtained.

Since these effects—especially the first one, which we have already signalled in a previous publication—may present some intrinsic interest, we have looked at them in more detail. To illustrate the first effect, Fig. 5 shows DLTS spectra taken on five different GaAs layers with all samples mounted at the same time under identical conditions in the crystal. The reproducibility of the temperature measurement is within 1 °C. Two different positions of the peak may be clearly seen. Most of the layers (including the one of Fig. 3) behave as samples (a), (d), or (e), while (b) and (c) have a larger emission rate, in spite of the fact that they are in fact less doped—thus, excluding the possibility of electric-field-assisted emission. We stress again that for all these GaAs samples the emission transient is rigorously exponential.

The temperature difference obtained between the two groups of GaAs samples is of the same order as the one measured between GaAs and $Ga_{0.95}In_{0.05}As$ (Fig. 3); therefore, one must be careful

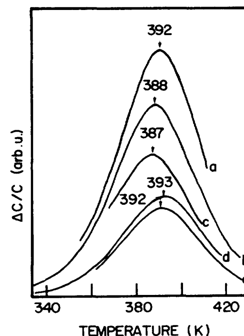

FIG. 5. Emission-rate variations from sample to sample in GaAs. Doping levels are (a) 1.5× 10^{15} cm^{-3}, (b) and (c) 8.10^{14} cm^{-3}, (d) and (e) 2.10^{15} cm^{-3}. All samples are VPE layers. The spectra were taken with all samples mounted simultaneously and identically in the cryostat. Reverse bias 5 V, emission window 120 s^{-1}.

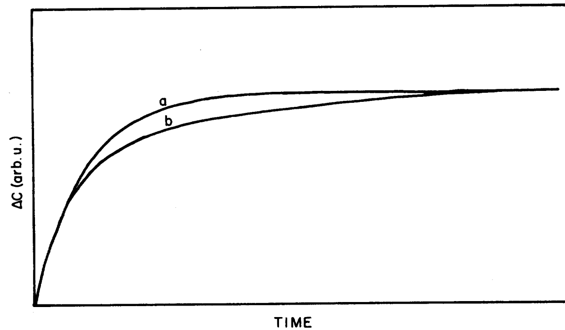

FIG. 6. Linear plot of capacitance transients at 27 °C. (a) GaAs, (b) ternary ≠ 1 (x = 0.046).

not to rely too heavily on the exact position of experimental points in Fig. 4.

These small emission-rate variations may be due to the effect of internal crystal strain.

The second "secondary effect" (nonexponential emission transients) has been observed to date only on the ternary samples. To look at this aspect more carefully, we performed accurate measurements at a fixed temperature, using the calculator system as transient averager in order to improve the signal-to-noise ratio. Typical observations are shown in Figs. 6 and 7. In Fig. 6, we plot in linear scales the transients observed at 27 °C for GaAs and for layer ≠1 (x = 0.5). In the second case, the nonexponential variation is easily seen.

In Fig. 7, we show semilogarithmic plots for three transients. Generally it appears feasible to describe the experimental curve as a sum of two or three pure exponentials. However, we have not been able to determine a regular variation of each time constant as a function of temperature, which would have conferred a physical meaning to this decomposition.

This completes the description of the secondary

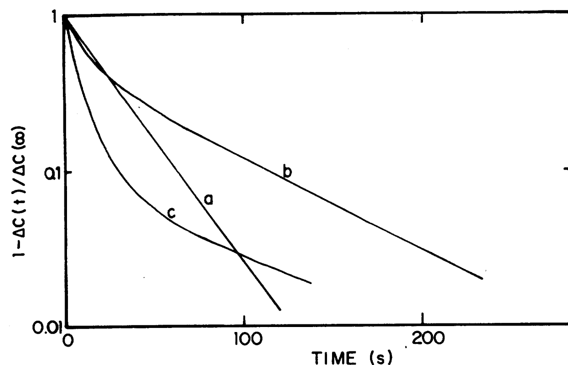

FIG. 7. Semilog plot of capacitance transients. (a) GaAs at 27 C, (b) ternary ≠ 1 at 27 C, (c) ternary ≠ 2 at 24 C.

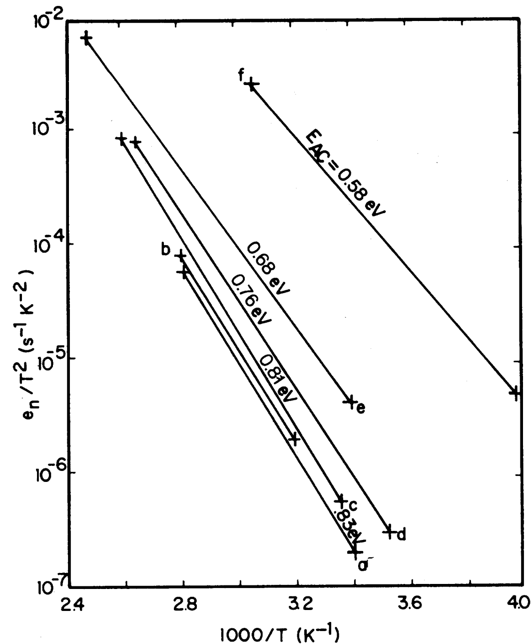

FIG. 8. Arrhenius plots of experimental emission rates of electron trap *A* vs temperature. (a) GaAs, standard; (b) ternary ≠ 1 (x = 0.046); (c) GaAs, high-emission-rate layer (see text); (d) ternary ≠ 2 (x = 0.077); (e) ternary ≠ 4 (x = 0.14); (f) ternary ≠ 5 (x = 0.21).

effects which loaded our investigation. In spite of these difficulties, from the DLTS data taken with different emission-rate windows it has been possible to obtain straight-line plots of $e_n/T^2 = f(1/T)$, characteristic for the deep electron trap A in alloys of increasing indium fraction. These are shown in Fig. 8. According to the discussion above, curve (b) for the ternary with weak indium content, falls within the range of uncertainty observed for pure GaAs. It would then be pointless to seek for better accuracy in the position of curve (b).

The activation energies E_{AC} associated with the plots of Fig. 8 are marked in this figure. They remain more or less constant for indium fractions lower than 8%, then start decreasing. It is known that these activation energies are related to the energetical difference between the conduction band and the deep level, $E_{IC} = E_C - E_T$. However, as discussed by Henry and Lang a correction E_B due to the variation of capture cross section versus temperature must be applied:

$$E_{AC} = E_{IC} + E_B . \quad (1)$$

Therefore, before comparing the experimental results to the theoretical predictions concerning E_{IC}, it is necessary to measure the capture cross sections and detect possible variations of E_B as a function of x.

2. *Electron-capture rates and cross sections*

The capture cross sections were obtained using either dynamic or static measurements of the capture rates.

The dynamic method consists of sweeping across the DLTS peak with different durations of the refilling pulse, their plotting the peak amplitude versus pulse duration. This method can only be used within a limited temperature range where the emission rate is not too small so that a DLTS peak is obtained in a reasonable time.

At lower temperatures, the capture rate may be obtained by the static method, provided that the deep level under study is the only one present—which has been shown above to be the case for our samples, Fig. 3—and provided that the trap concentration is sufficient so that the corresponding ΔC is well above the noise level. In the static measurement, one empties the trap by heating the sample under reverse bias, then one cools it down to the desired temperature; when this is reached a succession of refilling pulses of equal duration is applied and a capacitance reading is taken after each pulse.

Irrespective of the measuring method, if $N_t \ll n$ one expects the capacitance variations to follow an exponential dependence on refilling time. We have found, however, that the variations we observed were more complex, even in the case of pure GaAs as shown in Fig. 9. The reason for this behavior is not clear. We indicate in Fig. 9 that the experimental curves can be described as sums of two pure exponentials with approximately equal amplitudes. This of course suggests the successive capture of two electrons. Although this hypothesis should not be ignored, for the needs of the present study we have decided to circumvent the difficulty simply by taking, as a measure of the refilling time constant, the duration

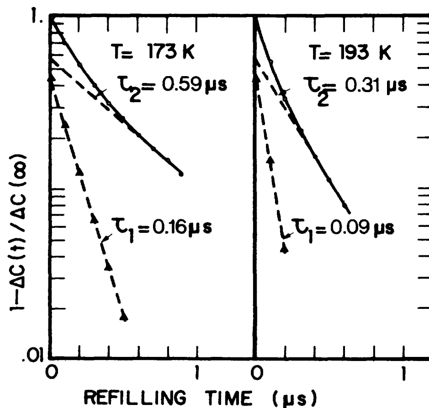

FIG. 9. Illustrating the nonexponential character of trap refilling in GaAs sample.

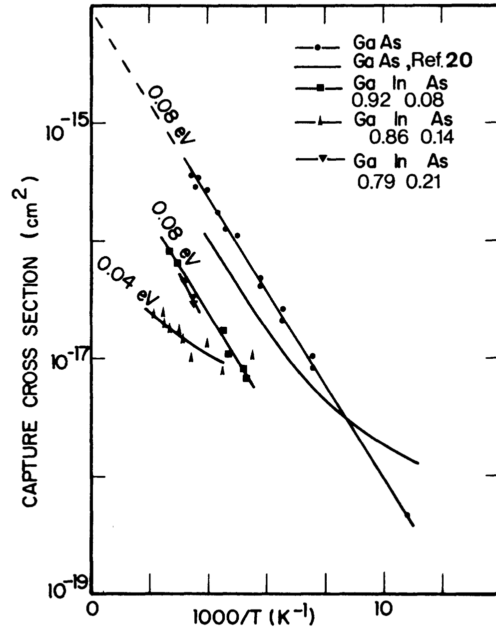

FIG. 10. Capture cross section vs inverse temperature for electron trap A in $Ga_{1-x}In_xAs$.

necessary for reducing the capacitance variation to $1/e$ of its initial value. The reasons for this are: (i) the ratio between the two time constants in Fig. 9 is not very large; (ii) this ratio does not seem to vary with temperature; (iii) as shown above, the *emptying* process is strictly exponential, at least in pure GaAs, tending to discourage the idea of a two electron trap. We have been able to obtain capture cross-sections σ_n for GaAs and for three alloy compositions—samples ≠51, 55, and 62 of Table I. When calculating σ_n from the capture rates, we have neglected the weak variation of electron effective mass versus x, using in all cases the same expression of the thermal velocity v_{th}

$$v_{th}(\text{cm/s}) = 2.6 \times 10^6\ T^{1/2}(K)\,. \tag{2}$$

The $\sigma_n(T)$ results are gathered in Fig. 10. For comparison, we have reproduced in this same figure the curve found by Lang and Henry[20] for GaAs. In view of the above discussed difficulties, the agreement seems satisfactory. In particular, the slope (activation energy E_B) of 0.08 eV is the same for the two series of experiments on GaAs.

The change induced in the capture cross sections by the increase of indium fraction x is remarkable. Up to $x = 0.14$, σ_n decreases by a large factor. For the sample with $x = 0.077$, the activation energy E_B is still essentially the same as in GaAs, but for the sample $x = 0.14$ it has decreased significantly, so that the two curves cross at low temperatures. Finally the (unfortunately very limited) data that

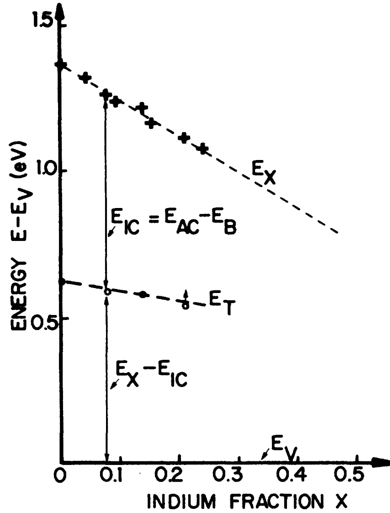

FIG. 11. Dependence on indium fraction x of the bottom of the conduction band E_c and of the deep level E_T for electron trap A. Reference is top of the valence band.

we have been able to get for $x = 0.21$ seem to indicate that σ_n increases again, but this point may need further verification.

C. Ionization energies

From the above data on emission activation energy E_{AC}, Fig. 8, and capture cross-section activation energy E_B, Fig. 10, we calculate the ionization energy E_{IC} of deep electron trap A as a function of indium fraction x, according to Eq. (1). The result is presented graphically in Fig. 11, where we plot both the band gap E_x (as from Table I) and $E_x - E_{IC}$ vs x. As suggested by the arrow pointing upwards, the point at $x = 0.21$ is probably an inferior limit, since E_B could not be reliably estimated in this case, so that we have simply taken $E_{IC} \simeq E_{AC}$.

The simplest smooth-curve approximations to the data, both for the conduction band and the deep level, are straight lines. From $x = 0$ to $x = 0.20$, the band gap varies by 18%, while $E_x - E_T$ varies by only 9%; that is to say, as x increases the deep level tends to come nearer to the conduction band.

This completes the description of experimental work. In Sec. IV, the results will be compared with theoretical predictions.

IV. CALCULATIONS OF DEEP-LEVEL STATES

A. Energy level of oxygen in GaAs

In previously reported[21] deep-level calculations, we have found an ionization energy of 0.78 eV for GaAs:O, in good agreement with the experimental data discussed in Sec. II above. Clearly the results reported here for $Ga_{1-x}In_xAs$ give us an opportunity to put the above hypothesis to a test; if the close agreement between the activation energy for trap A and the calculation for GaAs:O is not mere coincidence, then a similar agreement must exist in $Ga_{1-x}In_xAs$. Although this calculation cannot prove that trap A is due to oxygen (or any other chemical impurity), a disagreement between the calculated and observed activation energies in $Ga_{1-x}In_xAs$ might be a strong indication that the trap is not simple substitutional donor oxygen.

The details of pseudopotential calculations of impurity levels associated with deep traps in GaP and GaAs have been described in our previous publications[21,22] and will not be repeated here. The essence of the method consists of writing the impurity wave function ψ as an expansion in terms of the unperturbed Bloch functions of the host crystal, $\mathcal{S}_{n_1\vec{k}}$. Here n, $\vec{k}$ indicate the band and reduced wave vector, respectively. The one-electron Schrödinger equation, i.e.,

$$(H_0 + h)\psi = \epsilon\psi \tag{3}$$

with

$$\psi = \sum_{n_1,\vec{k}} A_{n,\vec{k}} \mathcal{S}_{n,\vec{k}} \tag{4}$$

is then solved numerically. The functions $\mathcal{S}_{n,\vec{k}}$ are obtained from a local empirical pseudopotential band-structure calculation.[23] Here h is the impurity pseudopotential which in this particular case is just the difference between the self-consistent (screened) pseudopotentials of oxygen and arsenic. The expansion in (4) requires ten bands and several thousand sampling points in the reduced zone to converge.

When we come to consider oxygen in $Ga_{1-x}In_xAs$

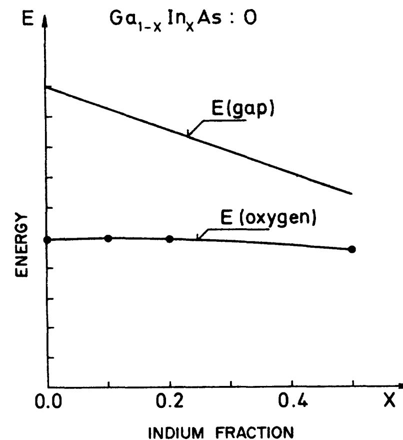

FIG. 12. Calculated ground-state energy of a single donor oxygen in $Ga_{1-x}In_xAs$. The position in the direct gap is shown.

for $x \neq 0$, we maintain our sampling procedure and the potential h unchanged. The band-structure parameters, i.e., the functions $\mathcal{S}_{n,\vec{k}}$ and energies $E_{n_1\vec{k}}$ are obtained as before, i.e., by solving

$$H_0 \mathcal{S}_{n,\vec{k}} = E_{n,\vec{k}} \mathcal{S}_{n,\vec{k}} . \tag{5}$$

The crystal potential H_0 for the alloy is set up according to the virtual-crystal approximation. This involves simple linear interpolation of the lattice constant and the pseudopotential form factors between GaAs and InAs values. The calculations were performed for $x = 0.0$, 0.1, 0.2, and 0.5 and the results are shown in Fig. 12. This figure shows both the calculated direct band gap and the impurity-ground-state energy as a function of the indium concentration x.

B. Comparison of theory with experiment

Comparison of the calculated (Fig. 12) activation energies with the experimental ones in Fig. 11 is not favorable enough and can hardly support our hypothesis that the trap is O donor at the As site. We must now closely examine our results in the light of all existing experimental information, for there may be evidence which might contradict our conclusions about the activation energy or some consequences of such a conclusion. However, before we do so we must critically assess the calculation itself.

As we have pointed out earlier,[21] the absolute position of an impurity level in the forbidden band gap is very difficult to calculate accurately. This is because the impurity-ground-state energy arises as a result of cancellations which take place when contributions coming from different parts of the wave-vector space are added up. Convergence properties of such a system are difficult and tedious to study. Furthermore, our calculation is not self-consistent in the usual sense and the reliability of the potential h depends to some extent on the validity of linear screening approximation. The close agreement of our theory with experiment as far as GaP:O is concerned must be at least to some degree fortuitous. In GaAs, the precision with which we can position a deep donor level can only be lower. The density of states near Γ_1 (conduction band) is very low and our sampling procedure does not really represent this part of the band structure very well. Fortunately, the ground-state wave function spreads over a large area in k space[21] and such parts as Γ_1 affect the ground state only very little. Positions of deep levels in the gap merely reflect a change in those parts of the band structure where the density of states is high. This argument which is not difficult to accept on intuitive grounds, has been well supported by all our calculations. Finally, the details of the band structure are not well described by the local empirical pseudopotential employed here. For instance, some very recent experiments[24] show that the secondary conduction-band minimum at X_1 is above that at L_1 (0.475 and 0.285 eV above the bottom of the conduction band of GaAs, respectively). Since we really calculated the impurity energy with respect to the lowest conduction-band valley with large density of states more accurately than with respect to Γ_1, all impurity energies shown in Fig. 12 should be reduced by about 50 meV. We do not believe that such corrections are of importance here since (a) they only represent a *systematic* error, and (b) this error is smaller than the expected (systematic) error due to sampling and impurity potential which amounts to at least ±0.1 eV.

We shall now concern ourselves with the *relative* changes in the ground-state energy. In Fig. 13, we can see the changes in the positions of the secondary minima at X_1 and L_1 as a function of x. A glance at Figs. 12 and 13 shows that—as expected—E (oxygen) does not follow the band edge but seems to "follow" the valence band. What really happens is that this level which is primarily associated with the conduction band[21] simply is not very sensitive to the low density of states area near Γ_1.

Of course, as x increases, the interaction with the Γ_1 valley should slowly increase in importance since Γ_1 comes closer to the level in the gap.

There is some uncertainty as far as the positions of X_1 and L_1 with respect to Γ_1 in InAs are concerned. Obviously, the relative change in the position of the deep level with x does depend on the change at X_1 and L_1. Hence, our predictions concerning the relative change in E(oxygen) also contain some uncertainty. However, the main result of our calculation, namely, that E(oxygen) does not follow either X_1, L_1, or Γ_1 and that $E_V - E$(oxygen) ≈ (const) for $x = 0.0–0.2$ (i.e., the range in which the experiment was performed), can hardly be altered by the above consideration significantly enough to render comparison with the experiment impossible. On the other hand, it may be argued

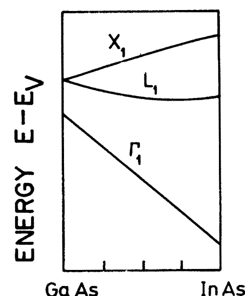

FIG. 13. Position of the conduction-band minima with respect to the top of the valence band in $Ga_{1-x}In_xAs$ from a simple virtual-crystal model employed in this calculation.

that the above behavior of E(oxygen) is not necessarily peculiar to oxygen. All deep states of this symmetry, dominated by short-range potentials, should be expected to follow such a trend, and it may well be beyond the sensitivity of our impurity calculation to distinguish one from another if only a small range of concentrations is studied. Recent work by Lang *et al.* on $Ga_{1-x}Al_xAs$ (Ref. 3) does confirm that the changes in trap energies with concentration x may indeed be small compared to the magnitude of the change of the direct gap. However, they also found that some levels of different depth exhibited a very similar change with alloy concentration.

In our calculation, we represent the crystal potential by an average potential obtained from a linear interpolation procedure. The samples used in the present experiment do not show any bowing in the band gap versus indium fraction variation. It has been pointed out[25] that in a high-quality $Ga_{1-x}In_xAs$ alloy, the bowing should indeed be negligible. The observed direct gap agrees well with the values calculated with our simple virtual-crystal model. Although this does not necessarily mean that there is no local disorder in the impurity cell, our calculations ignore any such correction. If the center is really the simple oxygen donor then such a correction should not be very important. Our studies[21] on the substitutional single donor oxygen in GaP certainly indicated that the ground state is s-like and insensitive to small asymmetric fields. An axial complex, on the other hand, may respond sharply[26] to small changes in the local environment which may be a function of the concentration x. Since several of the deep traps observed by Lang *et al.*[3] do not follow the trend predicted by our calculation for a symmetric center, our result might be taken as an indication that those centers are of lower symmetry.

As concerns our trap A, the observed variation in the impurity energy $E \equiv E(x)$ with respect to the valence band, is too fast to be consistent with our simple model (i.e., substitutional single donor oxygen), as can be seen from Figs. 11 and 12.

C. Discussion of the photoionization data

The photoionization spectrum of O-doped GaAs was shown in Fig. 1, and in Sec. II above, we argued that only the threshold in the middle of the gap, i.e., electron trap A, should be related to oxygen, the upturn above 1 eV being mainly a contribution from another level, with possibly some contribution due to the rise in the density of states in the GaAs conduction band[27] (Fig. 14). It is unfortunate that the presence of the second level masks this last contribution, since the exact knowledge of this part of the "oxygen" spectrum would greatly help the comparison with theory.

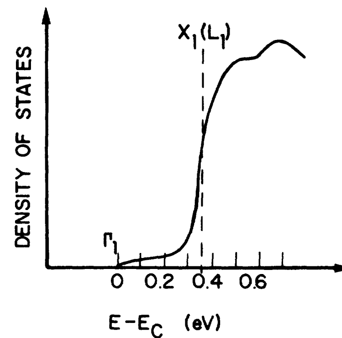

FIG. 14. Rough graph indicating the density of states near the bottom of the conduction band of GaAs.

At this point a comment on the problem of interpretation of this kind of data may be in order. It is remarkable that in spite of great importance generally attached to experimental information concerning optical cross sections for deep levels, the theoretical aspects of the problem have been largely neglected. Nevertheless, it has been shown[27] that simple extensions[28] of the well-known effective-mass theory do not apply in many cases. The experimental work of White *et al.*[29] confirms these theoretical considerations. In brief, there are at least three important points that must be taken into consideration:

(i) The wave function spreads over a large area in the wave-vector space and the optical matrix elements are significantly altered, if this fact is taken into account.

(ii) The details of such a process are particularly important in direct-gap materials where not only the position of the maximum of the frequency-dependent cross section, but also its shape near the threshold are affected.[27] Because of the low density of states at the conduction-band edge, the true threshold of the cross section associated with a particular level may be obscured by a combination of the above-mentioned effects and temperature-dependent phonon broadening.

(iii) Finally, one may expect a Franck-Condon shift of the order of 0.1 eV.

Our calculations showed that oxygen donor in GaAs is basically of similar nature as that in GaP. It is borne in mind that if such a center really exists, then it is capable of binding two electrons as well as its analog as in GaP.[21] We did not carry out a full-length analysis of the two-electron problem in GaAs, as we had done for GaP, and are not able to offer a numerical result for the Franck-Condon shift and the equilibrium energy of the two-electron state. However, as far as calculations are concerned, the degree of similarity between

GaP:O and GaAs:O is so great that a rough prediction can be made without going through the tedious and imperfect process of the numerical procedure. Thus for GaAs:O we might expect $E_2^0 \sim 0.6$ and $E_2^1 \sim 1.0$ eV (E_2^0 and E_2^1 are energies per electron in the two-electron state before and after the lattice relaxation takes place, respectively). The presence of a two-electron state may affect the observed optical spectra and it would be worth investigating whether the above mentioned two-electron state exists in $Ga_{1-x}In_xAs$.

D. Discussion of the electron-capture cross sections in $Ga_{1-x}In_xAs$

In Sec. III, we described our results concerning the electron-capture cross sections and their temperature dependence in $Ga_{1-x}In_xAs$. The main features of the temperature dependence of the cross section can be understood[20] with the help of a simple diagram in Fig. 15. The temperature dependence is dominated by an exponential factor $\exp(-E_B/kT)$. In GaAs, E_B for the level A is 80 meV. The exponential dependence is clearly seen in both Lang's and our data. In the alloy, the exponential behavior persists over a similar range of temperatures (Fig. 10). However, the barrier energy E_B changes when x is larger than 0.10. Hence, there are two important questions to ask: (i) How do we explain this variation of E_B v .h x? (ii) Is it consistent with our hypothesis ab the origin of the trap? However, the very fact that this capture mechanism is so important in $Ga_{1-x}In_xAs$ raises a question. The properties of the single donor oxygen in GaP have been studied experimentally by many authors. Yet we do not know of any report suggesting that the nonradiative capture mechanism—which is characterized by the exponential temperature dependence—is important for GaP:O. Only when a second electron is captured at that center do we observe the above-mentioned behavior. Why should a single donor oxygen in GaAs be so different from that in GaP? The impurity potentials, the wave functions, and the activation energies are very similar. The symmetry is the same in both cases. In brief, we can see no simple reason why a single donor oxygen in GaAs should exhibit the observed capture cross section. Of course, in the absence of a truly quantitative description of the nonradiative capture mechanism which would relate the values of E_B to the band-structure and impurity parameters, no definite conclusion can be made about the plausibility of our hypothesis. We feel, however, that the above contradiction perhaps gives the strongest hint that the trap A is of more complex nature.

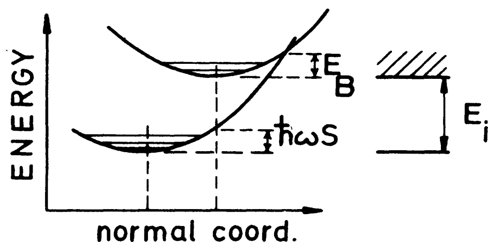

FIG. 15. Configuration coordinate diagram illustrating a capture proeess of a carrier from the conduction band into a deep level of energy E_i. S is the Franck-Condon shift expressed in units of lattice vibration.

Clearly the variation of E_B with x can only be explained in terms of the simple model pictured in Fig. 15 if we assume that the force constants in the impurity cell change with x. In view of the magnitude of the change in E_B, such a correction might be significant enough to affect the impurity energy not only via the band structure, but also via the impurity potential itself. It would also be interesting to know whether the results obtained in this study are peculiar to trap "A" or whether the barrier changes in a similar way for other deep traps, since it may well be that E_B is very sensitive to a small change in the force constants. The change in E_B with x—if E_B is indeed due to the same trap for all concentrations—amplifies our earlier conclusion that the trap A may possess lower symmetry.

V. SUMMARY

Transient-capacitance spectroscopy was applied to the study of the main electron trap A in vapor-phase epitaxial $Ga_{1-x}In_xAs$ alloys with $0<x<0.21$. Emission rate versus temperature and electron-capture cross section versus temperature data were obtained as a function of x. From these results, the ionization energy $E_c - E_t$ was determined as a function of x.

The experimental evidence relating this electron trap to the presence of oxygen was discussed, and new photoconductivity data taken directly on GaAs vapor-phase epitaxial layers with the substrate removed were presented to show the identity between this trap and the deep level observed in oxygen-doped bulk-grown material.

Theoretical calculations using the pseudopotential method were performed concerning the energy level of oxygen, substitutional on As site, in GaInAs alloys. Due to a combination of contributions from the Γ and the L (or X) minima in the conduction band, which vary in a different way as a function of x, the deep level tends to remain at a more or less constant energy difference with respect to E_V. This conclusion is not in good quantitative agreement with the experimental results. How-

ever, this argument alone does not allow to reject the hypothesis that the trap A is due to substitutional donor oxygen.

The experimental electron-capture cross sections in GaInAs show an exponential variation with inverse temperature, typical for the multiphonon emission capture mechanism. The cross sections decrease in magnitude as x increases, at least up to $x = 0.15$, and a variation of the activation energy E_B is also observed above $x = 0.10$. These rather remarkable results are discussed from the theoretical point of view; it is pointed out that, at least at the present state of knowledge, the multiphonon emission mechanism should *not* apply to single donor oxygen. Moreover, since the s-like wave function associated with the ground state of this defect should not be sensitive to small changes in the local environment due to alloying, the activation energy should not vary with composition as observed in our experiments. Therefore, we must conclude that the existing experimental evidence concerning this trap does not support the hypothesis that the trap is substitutional single donor oxygen.

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[1]T. Ikoma, M. Takikawa, and T. Okumura, in Proceedings of the 1976 International Conference on Solid State Devices, Tokyo, 1976 (unpublished).
[2]D. V. Lang, in Proceedings of the International Conference on Radiation Effects in Semiconductors, Dubrovnik, 1976 (unpublished).
[3]D. V. Lang, R. A. Logan, and L. C. Kimerling, Proceedings of the International Conference on the Physics Semiconductors, Rome, 1976 (unpublished).
[4]A. Majerfeld (private communication).
[5]A. Mircea and A. Mitonneau, Appl. Phys. 8, 15 (1975); A. Mircea, A. Mitonneau, L. Hollan, and A. Briere, *ibid.* 11, 153 (1976).
[6]D. V. Lang and R. A. Logan, J. Electron. Mater. 4, 1053 (1975).
[7]N. M. Kolchanova, G. N. Talalakin, and E. A. Kretova, Sov. Phys.-Semicond. 4, 174 (1970).
[8]M. Bleicher and E. Lange, Solid State Electron. 16, 375 (1973).
[9]H. G. Grimmeiss and L. A. Ledebo, J. Appl. Phys. 46, 2155 (1975).
[10]G. P. Peka, L. G. Shepel, and L. Z. Mirets, Sov. Phys.-Semicond. 7, 1439 (1974).
[11]A. Mitonneau and A. Mircea, Laboratoires d'Electronique et de Physique Appliquée, Internal Report No. J607, 1974 (unpublished).
[12]A. Mitonneau, G. M. Martin, and A. Mircea, *Proceedings of the Conference on GaAs Related Compounds*, Edinburgh, 1976 (The Institute of Physics, Bristol, 1977), Vol. 33a, p. 73.
[13]D. Bois and M. Boulou, Phys. Status Solidi A 22, 671 (1974).
[14]K. Sakai and T. Ikoma, Appl. Phys. 5, 165 (1974).
[15]A. Humbert, L. Hollan, and D. Bois, Appl. Phys. 9, 117 (1976).
[16]M. C. Boissy, D. Diguet, C. Schemali, and J. Hallais, in Ref. 12.
[17]J. S. Escher and B. F. Williams, J. Appl. Phys. 44, 525 (1973).
[18]A. Mitonneau, Philips Res. Rep. 31, 244 (1976).
[19]D. V. Lang, J. Appl. Phys. 45, 3023 (1974).
[20]D. V. Lang and C. H. Henry, Phys. Rev. Lett. 35, 1525 (1975).
[21]M. Jaros, J. Phys. C 8, 2455 (1975).
[22]M. Jaros and S. Brand, Phys. Rev. B 14, 4496 (1976).
[23]M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).
[24]D. E. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. Lett. 37, 766 (1976).
[25]B. J. Baliga, R. Bhas, and S. K. Ghandi, J. Appl. Phys. 46, 4608 (1975).
[26]M. Jaros and S. Brand, in Proceedings of the International Conference on the Physics of Semiconductors, Rome, 1976 (unpublished).
[27]M. Jaros, J. Phys. C 8, L264 (1975).
[28]G. Lucovsky, Solid State Commun. 3, 299 (1965).
[29]A. M. White, P. J. Dean, and P. Porteous, J. Appl. Phys. 47, 3230 (1976).
[30]A. L. Lin, E. Omelianovskii, and R. H. Bube, J. Appl. Phys. 47, 1852 (1976).