Pressure dependence of the $E2$ and $E1$ deep levels in GaAs, GaP, and their alloys

G. A. Samara, R. M. Biefeld, L. R. Dawson, T. E. Zipperian, and C. E. Barnes*
Sandia National Laboratories, Albuquerque, New Mexico 87185
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Measurements of the effects of pressure on the thermal-electron emission rate and capture cross section for the $E2$ and $E1$ deep levels in GaAs, GaP, and their alloys have yielded the pressure dependences of the energies of these levels, allowed evaluation of the breathing-mode lattice relaxations accompanying carrier emission or capture by these levels, and revealed trends that lead to new insights. The results are consistent with a model which associates $E2$ with the $(-/0)$ and $E1$ with the $(2-/-)$ charge states of the As (or P) vacancy.

Lattice defects are known to introduce energy levels into the band gaps of semiconductors, and these levels can have a strong influence on electronic properties and device performance. For this reason, the study of defects and their energy levels continues to be a very active area of semiconductor science. The increasing technological importance of the III-V semiconductors is refocusing attention on the need to understand their defect properties. Undoubtedly, the simplest defects in these materials are those which can be controllably introduced by relatively low energy ($\approx$ few MeV) electron, and gamma (γ) irradiation. Irradiation in this energy range produces single-atom displacements which can be expected to produce simple defects such as vacancies, interstitials, and close (Frenkel) pairs. Such irradiation is known[1-4] to produce a variety of deep electron levels known as $E1$, $E2$, $E3$, . . . , in the band gaps of GaAs, GaP, and their alloys. These levels have been studied extensively,[1-4] but the defects responsible for them remain largely unidentified.

Of the various E levels, the identification of $E1$ and $E2$ comes closest to being resolved. A large body of work has led to the following observations about these two levels.[1-4] (1) Their introduction rates and annealing kinetics are identical. (2) Their introduction rate is independent of temperature and has a threshold of 10 eV which is characteristic of the displacement of a single atom. (3) They do not depend on the kind and concentration of doping impurities. (4) Their concentration does not depend on x in $Al_xGa_{1-x}As$ ($0 \le x \le 0.47$). (5) They originate from the As sublattice. These observations strongly suggest that $E1$ and $E2$ are associated with the same defect. Theoretical considerations by Loualiche *et al.*[5] have suggested further that these two levels are associated with two charge states of the same intrinsic defect involving the As vacancy, V_{As}. The point is made[5] that this defect could be the isolated V_{As}, but a complex of V_{As} plus the arsenic interstitial, As_i, could not be ruled out. More recently, it has been proposed[1,6] that $E1$ and $E2$ are two charge states of V_{As}, namely, $E1$ is associated with the $V_{As^{2-}}/V_{As^-}$ state and $E2$ with the V_{As^-}/V_{As^0} state. As we shall see, the present results are consistent with this picture.

Earlier work has shown pressure to be a very useful variable in the study of deep levels providing insights into the physics, nature of deep-level potentials, and breathing-mode lattice relaxations accompanying emission and capture processes.[7-10] The expectation that pressure studies can provide new insights into the nature of $E1$ and $E2$ motivated the present work. Specifically, we have investigated the effects of combined hydrostatic pressure and temperature on electron emission and capture from the $E2$ deep level in $GaAs_{0.88}P_{0.12}$, $Al_{0.1}Ga_{0.9}As$, GaAs, and GaP and the $E1$ deep levels in $GaAs_{0.88}P_{0.12}$ and $Al_{0.1}Ga_{0.9}As$. This paper presents the results and their interpretation.

The levels were studied by transient-capacitance and deep-level transient-spectroscopy (DLTS) measurements on p^+-n junction diodes.[7] The diodes were fabricated from liquid-phase-epitaxy- and metal-organic chemical-vapor-deposition-grown samples with the following (p^+-n) doping levels: $GaAs_{0.88}P_{0.12}$ (1×10^{18} atoms Zn cm^{-3}/1×10^{17} Se cm^{-3}); $Al_{0.1}Ga_{0.9}As$ (1×10^{17} atoms Ge cm^{-3}/5×10^{15} cm^{-3}); GaP(2×10^{18} atoms Zn cm^{-3}/1×10^{16} cm^{-3}). Some data on the pressure dependence of $E2$ of GaAs are available in the literature.[11] The samples were chosen to explore effects due both to chemical substitution at both the Ga and As sites in GaAs and to differences in band structure. Specifically in this latter regard, for both $E1$ and $E2$ the emission is to the conduction-band minimum, and this minimum is at the Γ point of the Brillouin zone for the GaAs-rich samples and at the X point for GaP. The defects were introduced by γ irradiation (^{60}Co source) at room temperature to a total dose of $(1-2)\times10^8$ rad.

The experimental details were described earlier.[7] The measurements, performed in a pressure cell using helium as the pressure fluid, yielded the electron thermal emission rates (e_n), emission energies, and their pressure dependences. It is known that there is no energy barrier to electron capture by $E2$, and the same is believed to be true of $E1$.[1-4] We find that, to within experimental uncertainty, the electron-capture cross section (σ_n) is independent of both temperature and pressure.

The primary data generated in the present work are e_n

and σ_n and their pressure (p) and temperature (T) dependences. The data are analyzed and interpreted in terms of the detailed-balance result

$$e_n = \sigma_n \langle v_n \rangle N_c \exp(-\Delta G/kT)$$
$$= \sigma_n \langle v_n \rangle N_c \exp(\Delta S/k) \exp(-\Delta H/kT) , \quad (1)$$

following procedures discussed earlier.[7] Here $\langle v_n \rangle$ is the average electron thermal velocity, N_c is the effective density of states in the conduction band, and ΔG ($=\Delta H - T\Delta S$) is the change in Gibbs free energy which accompanies electron emission from the deep level. As will be shown later, for $E1$ and $E2$, σ_n is independent of pressure, and thus to a good approximation, Eq. (1) yields[7]

$$\left[\frac{\partial \ln e_n}{\partial p}\right]_T = -(kT)^{-1}\left[\frac{\partial \Delta G}{\partial p}\right]_T . \quad (2)$$

It is seen that measurements of e_n versus p at constant T yield $\Delta G(p)$, whereas measurements of e_n versus T at constant p plotted as $\ln(e_n T^{-2})$ versus T^{-1} at different pressures yield[7] $\Delta H(p)$. Finally, it can be easily shown that[7]

$$\left[\frac{\partial \Delta G}{\partial p}\right]_T = \Delta V , \quad (3)$$

where, in the absence of a barrier to electron capture (as is the case for the present levels), the thermodynamic volume change, or activation volume, ΔV, can be interpreted as the volume change, or breathing-mode relaxation, of the defect which accompanies electron emission. In using Eq. (3), the experimentally determined $(\partial \Delta G/\partial p)_T$ needs to be corrected for the hydrostatic deformation potential of the conduction-band edge, E_c, as discussed below.

The DLTS spectrum of these materials typically exhibits two sharp, widely separated peaks corresponding to electron emission from $E1$ and $E2$. Pressure causes relatively large shifts of both peaks. For the GaAs-rich samples, the shifts are to higher T's (Fig. 1), whereas for GaP the shifts are to lower T's. The difference is due to the fact that the band gap is indirect for GaP and direct for the other samples, and the deformation potentials of the Γ and X conduction-band edges have opposite signs. As we shall see later, when this qualitative difference is accounted for, the intrinsic pressure dependences are found to be qualitatively similar for all the samples.

Figure 2 shows typical Arrhenius plots of the emission rate, expressed as e_n/T^2, at different pressures for $E2$ of $GaAs_{0.88}P_{0.12}$. At constant temperature there is a large decrease in e_n with pressure which is due to the large increase in the $E2$ emission activation energy ($=\Delta H$) with pressure which is shown in the inset. For comparison, the inset also shows the pressure dependence of the emission activation energy for $E1$ for the same sample. Determination of σ_n from the initial capacitance amplitude after reverse bias and from the variation of the amplitude of the DLTS peak as a function of the length of the trap-filling pulse[7] showed that, to within experimental

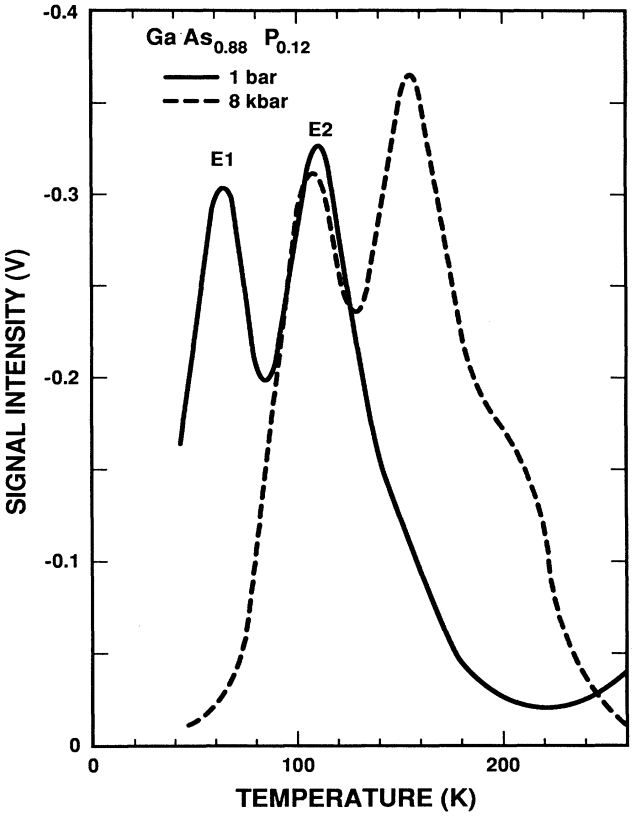

FIG. 1. DLTS spectra for $GaAs_{0.88}P_{0.12}$ at 1 bar and 8 kbar.

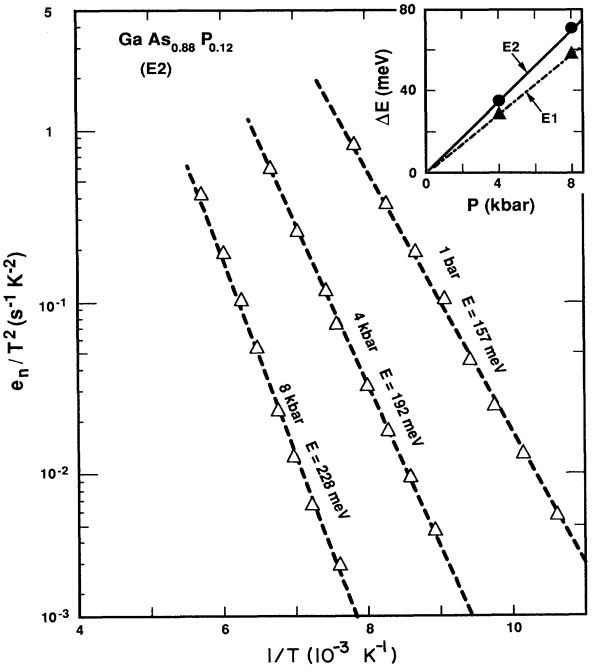

FIG. 2. Arrhenius plots showing the temperature dependence of the emission rate of electrons from the $E2$ level in $GaAs_{0.88}P_{0.12}$ at different pressures. The inset shows the pressure dependences of the emission activation energies for levels $E1$ and $E2$.

TABLE I. Isothermal measured (m) and intrinsic (i) pressure derivatives of the change in Gibbs free energy accompanying electron emission from the $E2$ and $E1$ levels for different samples. Also listed are the corresponding volume relaxations.

Material	Level	T (K)	$(\partial \Delta G/\partial p)_{T,m}$ (meV/kbar)	$(\partial \Delta G/\partial p)_{T,i}$ (meV/kbar)	ΔV (Å$^3/e$)	$\Delta V/V_0$ (%)
$Al_{0.1}Ga_{0.9}As$	$E2$	100	8.6±0.4	−2.2±1.7	−3.5±2.7	−5.7
$Al_{0.1}Ga_{0.9}As$	$E1$	100	6.6±0.5	−4.2±1.9	−6.7±3.0	−10.8
GaAs	$E2$		8.8[a]±0.2	−2.0±1.5	−3.2±2.4	−5.2
$GaAs_{0.88}P_{0.12}$	$E2$	115	8.0±0.2	−2.8±1.5	−4.5±2.4	−7.3
$GaAs_{0.88}P_{0.12}$	$E1$	85	7.1±0.4	−3.7±1.7	−5.9±2.7	−9.6
GaP	$E2$	140	−3.8±0.2	−3.2±1.5	−5.1±2.4	−9.3

[a]This result is taken from Ref. 11.

uncertainty, σ_n is independent of both temperature and pressure.

As already noted, ΔG represents the total-energy difference between the two different charge states (i.e., before and after emission) of the defect in their relaxed conditions. The isothermal pressure dependence of ΔG can be directly determined form the measured $e_n(T,p)$ data according to Eq. (2). Some of the results are given in Table I. The "*measured*" derivative $(\partial \Delta G/\partial p)_{T,m}$ (denoted by the subscript m) is only weakly dependent on T.

In interpreting the results, it is important to note that electron emission is measured from the deep level to E_c, so that E_c is the reference energy state relative to which the change in ΔG is measured. However, this reference energy state is not fixed; it is pressure dependent, and this dependence (which is represented by the hydrostatic deformation potential of E_c) contributes to $e_n(p)$, and thereby to $(\partial \Delta G/\partial p)_T$. It is necessary to correct for this contribution in order to determine the *intrinsic* effect, $(\partial \Delta G/\partial p)_{T,i}$, associated with the emission process. The intrinsic effect (denoted by the subscript i) represents the absolute shift of the level relative to a fixed reference and contains much of the physics which is relevant in comparing the different levels and in determining the breathing-mode relaxation accompanying electron emission or capture. In Table I we give both the *measured* and intrinsic values of $(\partial \Delta G/\partial p)_T$. We now discuss the correction procedure.

The hydrostatic deformation potential of E_c ($a_c = \partial E/\partial \ln V$) of GaAs (at the Γ point), which we take to also accurately represent the other two GaAs-rich samples in Table I, is large and reasonably well established. The most realistic theoretical and semiempirical determinations of a_c have yielded the following values (in eV per unit volume strain): −7.2,[12] −9.3,[13] −7.7,[14] −8.8,[15] and −9 to −10.[16] We take $a_c = -8.5 \pm 1$ eV to be a representative value. This value of a_c and the known compressibility of GaAs [$(-\partial \ln V/\partial p) = 1.27 \times 10^{-3}$/kbar] yield a pressure shift of E_c of $+10.8 \pm 1.3$ meV/kbar.

In the case of GaP, a_c is not known accurately enough. Two sets of values of a_c and of the valence-band hydrostatic deformation potential, a_v, are $a_c = 3.26$ eV and $a_v = 1.70$ eV,[12] and $a_c = 0.8$ eV and $a_v = -1.5$ eV.[15] Both sets overestimate the small known shift of the band gap[17] of GaP (−1.1 meV/kbar) by factors of ~1.5 and ~2, respectively. In view of the disparity in the a's, we have, for the purposes of the present analysis, assumed that the shift of the gap is taken up equally by E_c and E_v. This assumption and its implications for the present analysis can be easily reevaluated when more definitive values of the a's become available.

We now examine the results in Table I. Note that whereas $(\partial \Delta G/\partial p)_{T,m}$ is positive for the GaAs-rich samples and negative for GaP, this qualitative difference is entirely due to differences in the deformation potentials of E_c. The intrinsic effect, $(\partial \Delta G/\partial p)_{T,i}$, is negative for all the samples. This conclusion is independent of any uncertainties in deformation potentials. The negative sign implies that both $E2$ and $E1$ move higher in the gap (or energy) relative to a fixed reference. The relatively large uncertainties in $(\partial \Delta G/\partial p)_{T,i}$ and in the resulting ΔV's calculated via Eq. (3) result largely from the uncertainties in the E_c deformation potentials.

The ΔV's in Table I are also negative. A negative sign for ΔV implies that the lattice relaxes *inward* (i.e., contracts) upon electron emission from both $E2$ and $E1$. An *outward* relaxation of the same magnitude can be expected to occur on electron capture. The magnitudes of the ΔV's can best be appredicted by comparing them to the volume, V_0, of a sphere centered around a point defect with a radius equal to the Ga—As bond length in GaAs (2.45 Å) and the Ga—P bond length in GaP (2.36 Å). The ratio $\Delta V/V_0$, given in Table I, ranges from −5% for $E2$ of GaAs to over −9% for $E2$ of GaP and $E1$ of $GaAs_{0.88}P_{0.12}$ and $Al_{0.1}Ga_{0.9}As$. Thus, the relaxations are relatively large.

In addition to the negative signs of the $(\partial \Delta G/\partial p)_{T,i}$'s and ΔV's, the results in Table I reveal a number of trends in the magnitudes of these quantities which contain other insights into the nature of the defects involved. These trends are as follows. (1) A 10 at. % substitution of Al for Ga in GaAs has little effect on the response of $E2$. (2) A 12 at. % substitution of P for As in GaAs, on the other hand, significantly increases the magnitude of the response of $E2$. (3) The response of $E2$ is larger for GaP than for GaAs. (4) The response of $E1$ is considerably larger than that of $E2$.

As already noted, there is a body of experimental and theoretical evidence which makes it reasonable to believe that $E1$ and $E2$ are two charge states of V_{As} (or V_P). It

is well established theoretically[18] that V_{As} gives rise to two electronic energy levels—a lower level of a_1 symmetry which exists as a resonant state in the valence band and an in-gap, antibonding level of t_2 symmetry located in the upper half of the gap. The neutral As vacancy V_{As^0} is populated by three electrons, two in the a_1 level and one in the t_2 level. The additional electrons associated with V_{As^-} and $V_{As^{2-}}$ go into the t_2 level, and, by analogy with the well-understood vacancy in silicon, Jahn-Teller (JT) distortions can be expected to accompany the capture of these electrons. It has been proposed[1,2,6] that $E2$ and $E1$ are associated with the V_{As^-}/V_{As^0} and $V_{As^{2-}}/V_{As^-}$ levels, respectively. A schematic energy-level diagram for V_{As} is shown in Fig. 3.

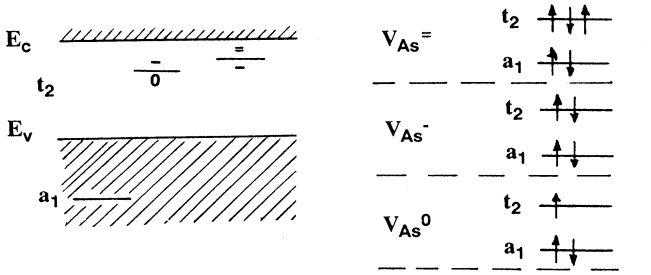

FIG. 3. Schematic energy-level diagram for the As vacancy in GaAs. The $E2$ and $E1$ levels studied in this work are believed to be associated with the singly and doubly charged t_2 levels of this vacancy. Both levels move higher in energy with pressure.

The present results are consistent with the association of $E2$ and $E1$ with the indicated two charge states of V_{As}. First, we note that trends (1) and (2) above point to the involvement of the As sublattice in the defect. Because both the $(-/0)$ and $(2-/-)$ levels are antibonding in character, compression of the lattice should shift their levels higher in energy. This is what we observe. Starting with V_{As^0}, electron capture into its antibonding state to form V_{As^-} can be expected to cause outward relaxation of the near-neighbor atoms to the vacancy. Subsequent emission of this electron should lead to the opposite effect, i.e., inward relaxation, or a negative ΔV, as observed. Additionally, the capture of the second electron into an already negatively charged antibonding state to form $V_{As^{2-}}$ should also cause outward relaxation, and the effect can be expected to be larger in magnitude than that associated with capture of the first electron. The larger inward relaxation we observe for emission from $E1$ compared with $E2$ is in accord with this expectation. The observed larger intrinsic energy shift of $E1$ with pressure [trend (4)] is also as expected from this model. It is thus seen that the present results are consistent with the proposed model. The results are also consistent with theoretical results[10] of the pressure dependence of deep levels in GaAs, which concluded that $E2$ moves higher in the gap and is associated with the As vacancy.

The ΔV's in Table I are the only quantitative values for the breathing-mode relaxation accompanying electron emission from any deep level in GaAs. Recent positron-annihilation (PA) results have been qualitatively interpreted to suggest an outward lattice relaxation accompanying the $V_{As^{2-}} \rightarrow V_{As^-}$ transition.[19] This is contrary to our findings. We believe that our method is more direct and accurate, whereas the interpretation of PA results in semiconductors is complicated and uncertain.[1] Furthermore, our method yields the breathing-mode relaxation, whereas PA presumably probes the total relaxation which includes effects due to the expected JT distortion.

Finally, we draw attention to trends (2) and (3) above, which show that the breathing-mode lattice relaxation accompanying electron emission from $E2$ is larger for the phosphorus-containing samples than for GaAs. We suggest that this result is most likely due to the increased ionic character of the bonding with increasing P content, it being a fact that GaP is more ionic than GaAs. Coulombic effects associated with electron capture or emission can be expected to be stronger for the more ionic host lattices. The trends indicated by the present results need to be studied for other compositions and for $E1$ in order to more fully test and quantify this proposed explanation.

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*Present address: The Jet Propulsion Laboratory, Pasadena, CA.

[1]See J. C. Bourgoin, H. J. von Bardeleben, and D. Stievenard, J. Appl. Phys. **64**, R65 (1988), and references therein.

[2]D. Pons and J. C. Bourgoin, J. Phys. C **18**, 3839 (1985), and references therein.

[3]D. V. Lang and L. C. Kimerling, in *Lattice Defects in Semiconductors,* Inst. Phys. Conf. Ser. No. 23 (IOP, Bristol, 1975), pp. 581 and 589.

[4]D. V. Lang, R. A. Logan, and L. C. Kimerling, Phys. Rev. B **15**, 4874 (1977).

[5]S. Loualiche *et al.*, Phys. Rev. B **30**, 5822 (1984).

[6]S. Loualiche, A. Nouailhat, and M. Lannoo, Solid State Commun. **51**, 509 (1984).

[7]G. A. Samara, Phys. Rev. B **36**, 4841 (1987); **39**, 11 001 (1989).

[8]W. Jantsch *et al.*, Phys. Rev. B **25**, 5515 (1982).

[9]M. Mizuta *et al.*, Jpn. J. Appl. Phys. **24**, L143 (1985).

[10]S. Y. Ren, J. D. Dow, and D. J. Wolford, Phys. Rev. B **25**, 7661 (1982).

[11]R. H. Wallis, A. Zylbersztejn, and J. M. Besson, Appl. Phys. Lett. **38**, 698 (1981).

[12]C. G. Van de Walle, Phys. Rev. B **39**, 1871 (1989).

[13]D. D. Nolte, W. Walukiewicz, and E. E. Haller, Phys. Rev. Lett. **59**, 501 (1987).

[14]L. Samuelson and S. Nilsson, J. Lumin. **40&41**, 127 (1988).

[15]M. Cardona and N. E. Christensen, Phys. Rev. B **35**, 6182 (1987).

[16]D. C. Look and P. C. Colter, Phys. Rev. B **28**, 1151 (1983).

[17]R. Zallen and W. Paul, Phys. Rev. **134**, A1628 (1964).

[18]G. B. Bachelet, G. A. Baraff, and M. Schlüter, Phys. Rev. B **24**, 915 (1981).

[19]C. Corbel *et al.*, Phys. Rev. B **38**, 8192 (1988).