PHYSICAL REVIEW B VOLUME 25, NUMBER 12 15 JUNE 1982

Pressure dependence of deep levels in GaAs

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(Received 9 February 1982)

The derivatives with respect to hydrostatic pressure of the deep energy levels associated with substitutional point defects in GaAs are evaluated and are found to be considerably smaller than the corresponding derivative of the fundamental band-gap energy. A deep level can be driven out of the gap by pressure, depending on its site, symmetry, and nearness to a band edge. The pressure dependence can be used to identify the site of a defect and the symmetry of its deep levels. A combination of the energy of a deep level, its pressure dependence, a theory of deep-level energies (which need be no more accurate than ± 0.6 eV), and the present theory eliminates all but a few point defects as candidates for producing a given level. In GaAs, $E2$ is assigned to an As vacancy, $E3$ and $E4$ are probably associated with defect complexes, and $EL2$ is very likely caused by either substitutional oxygen on an As site or As on a Ga site.

The purpose of this paper is to predict the hydrostatic pressure dependences dE/dp of substitutional deep point-defect levels in GaAs. We extend and refine previous theoretical work,[1,2] obtaining expressions for the pressure coefficient dE/dp which, for a defect at a specific site producing a level of particular symmetry, depends only on the energy of the level. We then show how these predictions can be combined with the Hjalmarson *et al.* theory of chemical trends for deep level energies[1] to eliminate typically all but a small number of the 116 possible sp^3-bonded substitutional point-defect assignments for a specific level.

We begin with the Schrödinger equation for the defect level E:

$$\det\left[V^{-1}-\int_{-\infty}^{\infty}dE'\frac{\delta(E'-H_0)}{E-E'}\right]=0\ , \tag{1}$$

where V is the defect potential operator, H_0 is the host Hamiltonian, and $\delta(E-H_0)$ is the spectral density operator of the host. For sp^3-bonded defects in a zinc-blende host, Hjalmarson *et al.*[1] have reduced this equation to two scalar equations by using the Vogl *et al.*[3] empirical sp^3s^* tight-binding theory of the host band structure:

$$(V_{l,b})^{-1}=\int dE'\frac{D_{l,b}(E')}{E-E'}\ . \tag{2}$$

Here b labels the site (anion or cation), and l labels the irreducible representation of the tetrahedral point group (T_d) and takes on values A_1 (s-like) and T_2 (p-like). In the theory of Hjalmarson *et al.*, the on-site perturbation potential $V_{l,b}$ is proportional to the difference in atomic l-orbital energies of the defect and the host, and $D_{l,b}(E')$ is the local spectral density, that is, the l,b projection of the host spectral density operator. In this paper we wish to determine dE/dp, the change in the energy E of a deep level induced by a change of applied hydrostatic pressure.

In the model of Vogl *et al.*, the diagonal matrix elements of H_0 and V are independent of the bond length. Thus we have[4]

$$\frac{dE}{dp}=\frac{\int dE'(E-E')^{-1}\frac{dD_{l,b}(E')}{dp}}{\int dE'(E-E')^{-2}D_{l,b}(E')}\ . \tag{3}$$

Observe that this expression does not depend explicitly on the difficult to determine[1,5] defect potential V; rather the pressure derivative depends only on the deep level's energy E, its irreducible representation l, and the site b. The properties of the host enter through the local spectral density $D_{l,b}$ and its derivative $dD_{l,b}/dp$, which can be evaluated using standard techniques.[1,5]

In order to evaluate the dependence on pressure of the local spectral density

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$$D_{l,b}(E)=\langle l,b,\vec{R}=\vec{0}\,|\,\delta(E-H_0)\,|\,l,b,\vec{R}=\vec{0}\rangle$$

we must construct the host-crystal Hamiltonian H_0 and determine its dependence on hydrostatic pressure (bond length).

In the empirical sp^3s^* model[3] of H_0 there are five localized basis orbitals per atom, resulting in a 10×10 Hamiltonian matrix at each wave vector $\vec{k}$. The diagonal matrix elements depend only on atomic orbital energies and do not change with pressure. The off-diagonal matrix elements of the empirical Hamiltonian $T_{\alpha,\beta}$ between orbitals on adjacent sites depend on the lattice constant a_L or bond length $d=\sqrt{3}a_L/4$ according to Harrison's rule,[6]

$$T_{\alpha,\beta}=T^{(0)}_{\alpha,\beta}(d_0/d)^{n_{\alpha,\beta}} ,$$

and hence are altered by hydrostatic pressure. In his elegant and global theory of semiconductors, Harrison chose all the exponents $n_{\alpha,\beta}=2$ after examining the trends in electronic structure from one semiconductor to another; subsequently Vogl *et al.* found that $n_{\alpha,\beta}=2$ was satisfactory for their global model as well.

Here we are more interested in the specific host GaAs than in the global trends from one semiconductor to another, and so we determine an improved tensor $n_{\alpha,\beta}$ for GaAs by fitting the observed pressure dependences of the direct band gaps at Γ, L, and X, and the indirect gaps from the valence-band maximum to L and X, using least-squares methods. The fit to these data is considerably better than that obtained by authors using second nearest-neighbor tight-binding theories that do not include the s^* basis orbital.[7-9] (See Table I; at all pressures we take the zero of energy to be at the valence-band maximum.) We find $n_{s,s}=4.144$, $n_{s,p}=n_{p,s}=2.341$, $n_{x,x}=2.596$, $n_{x,y}=2.220$, and $n_{s^*,p}=n_{p,s^*}=2.665$, where the subscripts refer to the s, p_x, p_y, and s^* orbitals. With these exponents determined from the pressure dependences of the energy gaps, it is straightfor-

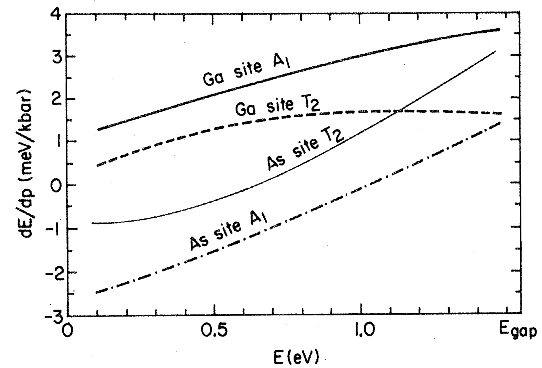

FIG. 1. Pressure derivatives dE/dp in meV/kbar for deep defect levels in GaAs, as functions of their energies E (in eV) in the band gap. The zero of energy is the valence-band maximum. The Ga-site A_1, Ga-site T_2, As-site T_2, and As-site A_1 levels are denoted by thick solid, dashed, thin solid, and chained lines, respectively. Note that the pressure derivative of the fundamental band gap, $dE_{\text{gap}}/dp=12.6$ meV/kbar, is much larger in magnitude than the pressure dependences of the deep levels.

TABLE I. Pressure derivatives, dE/dp, of the band gaps of GaAs in meV/kbar. The band gaps are labeled by the wave vectors in the Brillouin zone of the valence and conduction bands, respectively. For example, Γ, X labels the gap from the valence maximum at Γ to the conduction band at X.

Band gap	Γ,Γ	Γ,L	Γ,X	L,L	X,X
Experiment	12.6[a]	5.5[a]	−1.5[a]	5.0[b]	
	10.7−11.7[c,d]		−2.7[e]		
			−1.0[f]		
Theories					
Present work	12.6	4.4	−1.0	6.4	3.0
Osbourn (Ref. 7)	13.3	3.4	−0.4	5.2	3.1
Tsay *et al.* (Ref. 8)	13.3	6.2	+1.5	7.4	4.6
Camphausen (Ref. 9)	11.0	2.8	−0.8	4.5	3.6

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ward to determine $dD_{l,b}/dp$ and to evaluate dE/dp[4].

Our results for GaAs are given in Fig. 1, where we show the pressure derivatives dE/dp as functions of the substitutional deep trap energy E for A_1 (s-like) and T_2 (p-like) levels on the Ga and As sites. The present theory, unlike earlier work,[1] does not require a knowledge of the defect potential V; thus the site-diagonal contributions to V from spontaneous lattice relaxation around the defect and from the electron-electron interactions are implicitly included.

The predictions of Fig. 1 are in good general agreement with available data. For example, Wallis *et al.*[10] have studied the pressure dependences of a number of irradiation-induced deep levels in GaAs, and have found coefficients dE/dp (relative to the valence-band maximum) of 3.8, −0.9, and 2.1 meV/kbar for levels lying at 1.40, 1.19, and 0.92 eV, denoted $E2$, $E3$, and $E4$, respectively. Zylbersztejn *et al.*[11] have studied the 0.68-eV $EL2$ level (which occurs naturally in vapor-phase epitaxy material and is thought to be caused by oxygen) in the context of both earlier pressure-dependent photocapacitance studies by White *et al.*[12] and analyses of $EL2$ in $In_xGa_{1-x}As$ alloys by Mircea *et al.*[13] They conclude that $EL2$ experiences a significant, pressure-dependent Franck-Condon shift, and that dE/dp for this level is nearly zero. All of these levels have the approximate magnitudes for dE/dp predicted by the theory, values much smaller than dE_{gap}/dp. Moreover, the theory explains why the observations dE/dp are not monotonic functions of trap energy E: The defects are undoubtedly not all sp^3-bonded substitutional point defects on the same site producing levels of the same symmetry.

Interpretation of the pressure coefficient data is complicated by the fact that some of the levels, $EL2$ in particular, may experience significant pressure-dependent Franck-Condon shifts.[11] The resulting significant uncertainties in the pressure coefficients (of order $\simeq 1$ meV/kbar) preempt definitive assignments of the levels. Nevertheless it is possible, by making allowances for the uncertainties, to enumerate tentatively the substitutional point defects that might be responsible for the levels $E2$, $E3$, and $E4$. Without any theory, there are $116 = 29\times2\times2$ possible level assignments for each deep state, even if we restrict our attention to sp^3-bonded substitutional defects: vacancies or one of the 28 impurities from columns II*B* through VII of the Periodic Table: F, O, Cl, Br, N, S, Se, I, At, C, Te, P, As, Po, Sb, Ge, Bi, Si, B, Sn, Pb, Ga, Al, In, Tl, Zn, Cd, and Hg. These defects may occupy either the anion or the cation site and may produce levels of either A_1 (s-like) or T_2 (p-like) symmetry. The pressure dependence alone can be used to eliminate typically approximately 50% of the possible assignments; but when combined with even a quite inaccurate theory of deep levels, the pressure dependence can be used to further reduce the number of possiblities to typically one or two. In order to demonstrate this, we make the following assumptions: (i) The predicted pressure dependences of the deep levels $E2$, $E3$, and $E4$ disagree with experiment by less than 1.5 meV/kbar (our estimated theoretical uncertainty is 0.5 meV/kbar), (ii) the predictions of deep impurity levels by Hjalmarson *et al.* are in error by less than 0.6 eV, and (iii) the Hjalmarson *et al.* theory correctly reproduces the general trends in the relative ordering of defect levels. With these very generous assumptions and some knowledge of data, we reach the following conclusions concerning the deep levels $E2$, $E3$, and $E4$ in GaAs: (i) $E2$ is unlikely to be associated with a Ga vacancy but could be generated by an As vacancy, (ii) $E3$ is very unlikely to be produced by a substitutional sp^3-bonded point defect, and (iii) $E4$ could be caused by a complex involving an As vacancy.

$E2$ has a pressure dependence compatible with only Ga-site A_1 or As-site T_2 levels. If $E2$ is a Ga-site A_1 impurity level, the responsible defect must be more electronegative than Ge,[1] which is known to produce a shallow donor[14]; only Sb is predicted[1] to have a Ga-site A_1 level within 0.6 eV of $E2$. The only As-site T_2 defect level predicted to lie within 0.6 eV of $E2$ is the vacancy. We assign $E2$ to an As-vacancy T_2-symmetric level, because vacancies are more likely to be present than Sb impurities.

The pressure dependence of $E3$ rules out all substitutional sp^3-bonded defects, except, very marginally, an As-site A_1-symmetric level of a vacancy, F, O, Cl, or Br. Since the halogens are relatively insoluble, and this level lies above $EL2$, which we believe to be generated by substitutional oxygen, we assign $E3$ to an extended defect. This agrees with the conclusion of Pons *et al.*[15] that the annealing kinetics of the $E3$ defect are characteristic of a complex, possibly an As-vacancy—interstitial-As pair. An early suggestion[16] that $E3$ might be a Ga-vacancy level is ruled out both by the observed pressure dependence and by various theories,[1,17] all of which place this level near the valence-band

maximum or out of the gap.

$E4$ has a pressure dependence compatible with all assignments except an As-site A_1 level. However, its energy is compatible only with (i) an As T_2 vacancy, (ii) a Ga-site A_1-symmetric Sb level, and (iii) Ga-site T_2-symmetric levels of O, Cl, and Br (N and more electropositive defect levels are known to lie above the conduction-band edge[18]). Of these defects, only the As vacancy is even likely to occur in appreciable concentration; moreover, annealing studies[14] indicate that $E4$, like $E3$, is a defect complex—perhaps an As vacancy and an interstitial. The present work lends a modicum of support to that identification.

The pressure coefficient of $EL2$ is sufficiently uncertain because of the problem with Franck-Condon shifts that it does not provide a useful basis for eliminating possible defects. The conclusion that it is near zero is, of course, compatible with its (somewhat controversial[19]) identification as an oxygen substitutional center. Its energy is compatible with A_1-symmetric levels of an As-site vacancy, F (which is improbable), or oxygen, or Ga-site T_2 levels of O, Cl, Br, N, or S, or Ga-site A_1 levels of Se, I, At, C, Te, P, As, Po, or Sb. Of these, the oxygen identification is most reasonable, although C and As are possible. Independent evidence lends support to this identification: $EL2$ appears in GaAs intentionally doped with oxygen. The oxygen defect level in GaP, together with a theory of how it varies in $GaAs_{1-x}P_x$,[1] indicates that the GaAs oxygen level should lie near $EL2$.[1] Recent experiments on O in $GaAs_{1-x}P_x$ for $x > 0.6$ also extrapolate to $EL2$ for $x = 0$.[20] If the oxygen identification should turn out to be incorrect, the next most likely assignment is the native antisite defect: As on a Ga site. Thus we conclude that in GaAs the pressure dependence of the deep levels is extremely useful for identifying the defects that generate deep levels.

Several general features of dE/dp for GaAs are noteworthy: (i) dE/dp increases more or less monotonically from the valence-band maximum to the conduction-band minimum. (ii) The pressure derivatives dE/dp for the deep levels in the GaAs band gap are considerably smaller in magnitude than the corresponding derivatives for the fundamental band gap itself [$\simeq$1 meV/kbar vs 12.6 meV/kbar (Ref. 8)]. This means that resonances lying just outside the band gap can be driven *into* the gap by pressure. (iii) For anion site defects producing levels very near the valence-band maximum, dE/dp is negative, indicating that pressure

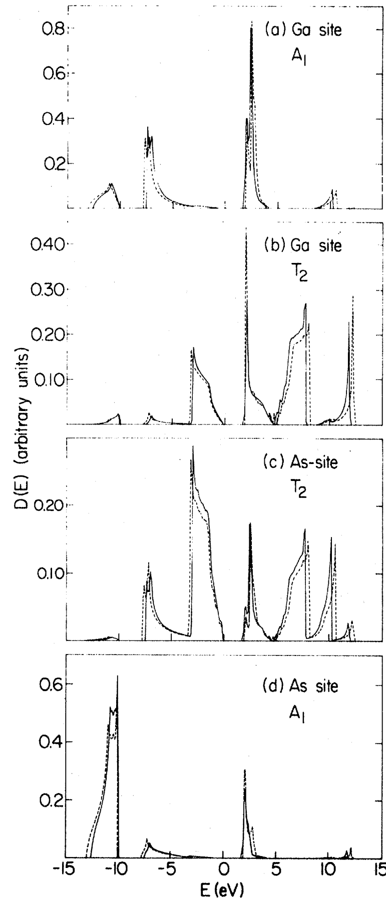

FIG. 2. Local spectral density $D_{l,b}(E)$ of GaAs (in arbitrary units) vs energy E (in eV) for (a) $l = a_1$, b = cation; (b) $l = T_2$, b = cation; (c) $l = T_2$, b = anion; (d) $l = A_1$, b = anion, both for zero pressure (solid line) and for 50 kbar pressure (dashed).

can drive these levels *out of* the gap; that is, pressure causes the deep level to move down in energy more than the valence-band maximum does.

These effects can be qualitatively understood by examining both the numerator of the right-hand side of Eq. (3) and the integrands $dD_{l,b}/dp$ depicted in Fig. 2. [The denominator of Eq. (3), being positive definite, does not affect the qualitative behavior of the levels in response to pressure.] The deep-level position in the gap is determined by the competition between the conduction-band states repelling the level downward and the valence-band states pushing it upward in energy. [See Eq. (2).] Similar considerations govern the level's response to pressure. [See Eq. (3).] Pressure increases the bonding-antibonding splitting between the valence- and conduction-band states in all cases (Fig.2). Hence the conduction-band states press down on

the deep level less and the valence-band states likewise repel it upward less. This competition determines whether the level moves up or down in energy (with respect to the valence-band maximum) when pressure is applied. The conduction band is largely Ga-like in character, and so tends to dominate the Ga-site defects, causing their levels to move toward higher energy with pressure, along with the conduction-band antibonding states. [See Figs. 2(a) and 2(b).] The situation for As-site defects is more balanced [Figs. 2(c) and 2(d)], and the denominator $E-E'$ of Eq. (3) provides a decisive influence. Deep levels close to the conduction-band edge are dominated by the conduction band, and like it, exhibit positive values of dE/dp. But levels near the bottom of the band gap do not feel the conduction band so strongly and can yield energies with $dE/dp<0$, characteristic of valence-band dominance.

We hope that these theoretical results will stimulate more experimental studies of the pressure dependences of deep levels.

We gratefully acknowledge the financial support of the Office of Naval Research (Grants Nos. N00014-77-C-0537 and N00014-80-C-0376). We thank the Department of Energy for the use of the Materials Research Laboratory computer (Grant No. DE-AC02-76-ER01198). Many of the ideas of this work grew out of earlier work and discussions with H. P. Hjalmarson, W. Y. Hsu, M. Jaros, T. C. McGill, O. F. Sankey, and P. Vogl.

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