Breathing-Mode Relaxation Associated with Electron Emission and Capture Processes of $EL2$ in GaAs

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Analysis of the effects of hydrostatic pressure on the electronic emission and capture properties of the (0/+) and (+/++) deep levels of the $EL2$ defect in GaAs leads to the following conclusions: (1) Both levels move higher in the band gap with pressure; (2) relatively large inward (outward) lattice relaxations accompany electron emission (capture) from (by) these levels; and (3) the magnitudes of the relaxations agree quantitatively with theoretical results which identify $EL2$ as the As antisite defect. These results which emphasize the antibonding character of the orbitals which describe $EL2$ are consistent with this identification.

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The midgap donor known as $EL2$ is the dominant deep electronic level in melt-grown and vapor-phase, epitaxially grown GaAs. It controls the electronic properties of semi-insulating GaAs by pinning the Fermi level, and its microscopic structure and metastability have been the subject of very extensive research [1–6]. There are two in-gap deep levels associated with the stable atomic configuration of $EL2$ [6]. The first corresponds to the first donor ionization state (0/+), is observed in n-type GaAs, and has an electron emission activation energy of 0.815 eV and a thermally activated electron capture cross section with energy barrier $E_b = 66$ meV. Thus, this level is located at $E_c - 0.75$ eV (where E_c is the conduction-band edge) as is also deduced from Hall measurements [6]. The second level corresponds to the second donor ionization state (+/++) and is observed in p-type GaAs. It has a hole emission activation energy of 0.54 eV and, presumably, no capture barrier [7], so that it is located at $E_v + 0.54$ eV (where E_v is the valence-band edge).

Although the preponderance of the evidence definitively points to the involvement of the As antisite defect (As_{Ga}) in its stable configuration, uncertainties still remain as to $EL2$'s exact microstructure. Currently, the two leading models [1–6] associate $EL2$ with either (i) the isolated As_{Ga} or (ii) a loosely bound As-antisite–As-interstitial (i.e., As_{Ga}-As_i) pair. The formation of either defect can be expected to lead to relaxation of the neighboring atoms, and additional relaxation should result from the emission or capture of electrons from the center. Both the signs and magnitudes of these relaxations are important to understanding the physics and microstructure of $EL2$. Recent theoretical calculations [2,4] have evaluated one or both of these relaxations for the As_{Ga} defect, but there are no experimental measurements.

Here we report the effects of hydrostatic pressure on the electron emission and capture properties of the (0/+) state, and use these results along with complementary earlier data to quantitatively evaluate the breathing-mode relaxations associated with the emission and capture processes for both the (0/+) and (+/++) states. The principal findings of the work are as follows: (i) There are relatively large inward (outward) lattice relaxations accompanying electron emission (capture) from (by) these two charge states of $EL2$, and the magnitudes of these relaxations agree quantitatively with the above-cited theoretical results which associate $EL2$ with the As_{Ga}; (ii) the sum of the combined relaxations accompanying emission from the two states (i.e., the emission of two electrons) is equal in magnitude (but is opposite in sign) to the theoretically deduced relaxation accompanying the formation of the As_{Ga}; and (iii) both levels move higher in the band gap with pressure.

In view of the importance of $EL2$ and of some differences in earlier pressure results [8–10] on the (0/+) state (possibly due to differences in samples used), we reinvestigated this state. We performed isothermal transient capacitance and deep-level transient spectroscopy (DLTS) measurements on gold Schottky barriers, obtaining the electron thermal emission rate (e_n), emission energy (E_n), preexponential factor (proportional to the electron capture cross section σ_n), and their pressure (P) dependences. Two types of samples were used and gave similar results: (i) bulk, Si-doped, liquid encapsulated Czochralski (LEC) grown GaAs samples and (ii) samples where the $EL2$ defect was confined to interrupted growth interfaces of thin metal-organic chemical vapor deposition (MOCVD) grown GaAs layers [11]. The experimental details were similar to those described earlier [12].

The data are analyzed and interpreted in terms of the detailed balance result $e_n = \sigma_n \langle v_n \rangle N_c \exp[-\Delta G_n/kT]$ following procedures discussed earlier [12]. $\langle v_n \rangle$ is the average electron thermal velocity, and N_c is the effective density of states in the conduction band. The product $\langle v_n \rangle N_c$ is proportional to $m_n^* T^2$, where m_n^* is the electron ef-

fective mass. The pressure dependence of m_n^* is negligibly small [12]. ΔG_n is the change in Gibbs free energy which represents the total energy difference between the two different charge states (i.e., before and after emission) of the defect. It can be expressed in terms of the enthalpy (ΔH_n) and total entropy (ΔS_n) changes accompanying electron emission, since $\Delta G_n = \Delta H_n - T\Delta S_n$. The above equation can be rewritten in the form $e_n/T^2 = A\sigma_n' \exp(-E_n/kT)$, where A is a constant ($=2.28 \times 10^{20}$ cm^{-2}s^{-1}K^{-2} for GaAs), σ_n' is the capture cross section multiplied by the entropy factor $\exp(\Delta S_n/k)$, and E_n ($\equiv \Delta H_n$) is the usual thermal emission activation energy. If σ_n is thermally activated with a barrier energy E_b, then $E_n = E_i + E_b$, where E_i is the ionization energy of the deep level.

The pressure dependence of the entropy factor is expected to be relatively small [12], and the pressure dependence of σ_n' should then reflect that of σ_n. From the pressure dependences of e_n and σ_n we can determine [11,12] $\Delta G(P)$. It can then be easily shown that [12] $(\partial \Delta G/\partial P)_T = \Delta V$, where ΔV is the thermodynamic activation volume for emission. In the absence of a barrier to electron capture, or after correcting for such a barrier, ΔV can be interpreted as the volume change, or breathing-mode relaxation, of the defect which accompanies electron emission [12]. Analogous equations apply for hole emission.

Figure 1(a) shows the temperature (T) dependence of the isothermal logarithmic pressure derivative of e_n.

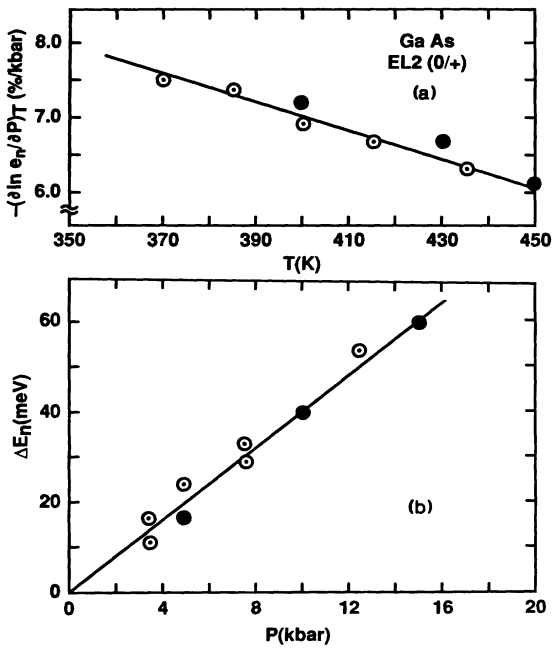

FIG. 1. (a) Temperature dependence of the logarithmic pressure derivative of the emission rate and (b) pressure dependence of the thermal emission energy, for the (0/+) transition of $EL2$. Symbols represent different samples.

Note that whereas this derivative decreases with T as shown, its product with T, which is $\propto (\partial \Delta G_n/\partial P)_T$, is essentially independent of T. These results were obtained from capacitance transients and from DLTS spectra as described earlier [12].

Figure 1(b) shows the directly measured shift with pressure of the (0/+) level relative to the conduction-band edge E_c determined from isobaric $\ln(e_n/T^2)$ vs $1/T$ plots [12]. The slope, $dE_n/dP = 4.1 \pm 0.5$ meV/kbar, is in good agreement with the earlier initial slopes [8,9] of 3.8 and 4.4 meV/kbar. We already noted that this level has a capture barrier E_b. The pressure dependence of E_b was determined from photoconductivity measurements [10] and is $dE_b/dP = -4.9 \pm 0.5$ meV/kbar. This value, combined with our result for $E_n(P)$, yields $dE_i/dP = 9.0 \pm 1.0$ meV/kbar for the shift of the ionization energy of the level relative to E_c.

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 ΔE and the change in ΔG are measured. However, this reference state is not fixed; it is pressure dependent, and this dependence (represented by the hydrostatic deformation potential a_c of E_c, i.e., $a_c \equiv \partial E_c/\partial \ln V$, where V is the volume) contributes to the measured pressure dependence of e_n, and thereby to $(\partial \Delta G/\partial P)_T$. It is necessary to correct for this contribution in order to determine the absolute (i.e., relative to a fixed reference) shifts, $(dE_i/dP)_{\rm abs}$ and $(\partial \Delta G_i/\partial P)_{T,\rm abs}$, associated with emission. It is these shifts which contain the physics.

For GaAs, $a_c = -8.9 \pm 1.0$ eV which, when combined with a volume compressibility of 1.27×10^{-3} kbar, yields $dE_c/dP = 11.3 \pm 1.0$ meV/kbar [13]. The absolute pressure derivative of the (0/+) level is then $(dE_i/dP)_{\rm abs} = dE_i/dP - dE_c/dP = -2.3 \pm 2.0$ meV/kbar. We take this value to also represent $(\partial \Delta G_i/\partial P)_{\rm abs}$; i.e., we neglect the pressure dependence of the entropy which should be relatively small [11,12]. The relatively large uncertainty in $(dE_i/dP)_{\rm abs}$ represents the sum of the uncertainties in the measured pressure derivatives of E_n, E_b and in the deformation potential. The actual uncertainty is undoubtedly much smaller. The various pressure derivatives and ΔV are summarized in Table I.

Recently Bliss *et al.* [7] measured the shift of the hole emission rate of the (++/+) level (relative to E_v) as a function of stress applied in the [100] and [110] directions in p-GaAs. There is no measurable stress dependence of the hole capture barrier (if such a barrier is at all present) for this level [7]. Analysis of the results, based on the use of -0.7 ± 1.0 eV (which is very close to the value deduced in Ref. [13]) for the hydrostatic deformation potential of E_v [14], yielded [7] 3.9 ± 1.5 meV/kbar for the absolute pressure dependence of this level which we take to represent the absolute value of $(\partial \Delta G_i/\partial P)_T$. These results and the associated ΔV are summarized in Table I.

TABLE I. Summary of the thermal emission activation energies (E_n), capture barrier energies (E_b), and their pressure derivatives, of the absolute pressure dependence of the change in Gibbs free energy upon emission (ΔG_i), and of the breathing-mode volume (ΔV) and bond length (Δr) relaxations for the two transitions of $EL2$.

Level	Process	E_n (eV)	dE_n/dP (meV/kbar)	E_b (eV)	dE_b/dP (meV/kbar)	$(\partial\Delta G_i/\partial P)_{abs}$ (meV/kbar)	ΔV (Å^3/e,h)	Δr (Å/e,h)
(0/+)	e emission	$E_c-0.75$	4.1 ± 0.5	0.066	-4.9 ± 0.5	-2.3 ± 2.0	-3.7 ± 3.0	-0.05
(++/+)	h emission	$E_v+0.54$	3.0 ± 1.0	0	0	$+3.9\pm1.5$	$+6.2\pm2.4$	$+0.08$

We now examine the results in Table I. First, note that whereas the measured derivative dE_n/dP for the (0/+) transition is positive, the absolute pressure derivative is negative. This is simply a consequence of the large positive pressure derivative of E_c. The negative value of $(dE_i/dP)_{abs}$ implies that the (0/+) level moves up in the gap relative to a higher-lying reference state since the electron emission is to the conduction band. The associated negative ΔV for this level implies *inward* breathing-mode lattice relaxation (i.e., contraction) on *electron emission*. An *outward* relaxation (i.e., expansion) of the same magnitude can be expected on *electron capture*.

For the (+/++) level, the experiment of Bliss *et al.* [7] on p-type GaAs examined *hole emission*, and, to emphasize this point, we designate the transition as (++/+) in Table I. The absolute pressure shift of this level is positive, implying that the level moves up in the gap relative to the lower-lying reference state which is the valence-band edge. The calculated ΔV in Table I is positive implying *outward* lattice relaxation on *hole emission* which corresponds to *electron capture*. An *inward* relaxation of the same magnitude can be expected on *electron emission*, i.e., for the (+/++) transition. Thus, the relaxation is inward for electron emission from both levels.

The results in Table I highlight the antibonding character of the wave functions which describe both levels. Compression of the lattice can be expected to shift antibonding energy levels higher in the gap, as observed. Additionally, electron capture into an antibonding state should cause *outward* relaxation of the near-neighbor atoms to the defect. Subsequent electron emission should lead to the opposite effect, i.e., *inward* relaxation, or a negative ΔV, as we find.

We now consider the implications of the above results. We shall concentrate on the association of $EL2$ with As_{Ga} because theoretical results exist on this defect for comparison. Optical experiments under uniaxial stress and magnetic field [1,5] have established that $EL2$ has tetrahedral T_d symmetry, thereby prompting the association of this defect with the isolated As_{Ga}. Theoretical calculations [3] supported this identification by ruling out As_i as a component of $EL2$ to the extent that the optical results are linked to $EL2$.

The As_{Ga} produces two states [4,15]: a deep in-gap bound state of A_1 symmetry and a state of T_2 symmetry which is resonant in the conduction band. On replacing Ga by As to form As_{Ga}, the two donor electrons of the As antisite occupy the antibonding orbitals in the A_1 state. The result is increased localization of the wave functions near the As atom and a weakening of the bonds of the antisite to its four As neighbors. Consequently, a radial outward relaxation of the four As nearest neighbors can be expected. For the (0/+) transition, one of the two A_1 electrons is emitted from the center thereby reducing the antibonding character and strengthening the bonding of the antisite to its As neighbors leading to inward relaxation. The (+/++) transition removes the second antibonding A_1 electron and should lead to additional inward relaxation.

With T_d symmetry, only breathing-mode lattice relaxation accompanies the formation of the As_{Ga} antisite. This fact along with the association of $EL2$ with As_{Ga} allows us to put the magnitudes and signs of the ΔV's in Table I into perspective. We compare the ΔV's to the volume V_0 (=61.6 Å^3) of a sphere centered at the antisite and of radius equal to the Ga-As bond length in GaAs, r_0 (=2.45 Å). The ratio $\Delta V/V_0$ is -6.0% for the (0/+) transition and -10.0% for the (+/++) transition. If to a first approximation we assume that all of the relaxation is taken up by the first shell of atoms around the defect, then a relevant measure of the deduced relaxations is the change in bond length $\Delta r/r_0$, $=\frac{1}{3}(\Delta V/V_0)$, which is -2.0% and -3.3% for the (0/+) and (+/++) transitions, respectively. The corresponding Δr's are -0.05 Å and -0.08 Å.

The approximation that all of the experimentally deduced ΔV is taken up by the first shell of atoms around the defect cannot, of course, be strictly correct, but it can be argued that it is approximately true [9]. For example, EXAFS results [16] on the relaxation of the GaAs lattice around substitutional S atoms show that the relaxation is largely taken up by the first-neighbor shell with "relatively unperturbed second- and third-neighbor shells."

With the emission of the two donor electrons from their antibonding states, the As antisite (i.e., As_{Ga}^{++}) should very nearly resemble neutral Ga (i.e., Ga^0), and the As-As bond length around the defect should reduce to the Ga-As bond length in GaAs. Thus, we expect the magnitude of the sum of the above two relaxations to be a good measure of the relaxation associated with the formation of the As antisite, namely, $\Delta r=+0.13$ Å (=0.05 +0.08), which is the opposite of the sign of Δr on emission of the two electrons.

Chadi and Chang's *ab initio* pseudopotential total-

energy calculations [2] revealed the antibonding character of As_{Ga} and showed that the four As neighbors relax outward by $\Delta r = 0.19$ Å on antisite formation. Similar more recent calculations by Caldas *et al.* [4] yielded $\Delta r = 0.12$ Å. The excellent agreement of this latter value with our experimentally deduced $\Delta r = 0.13$ Å is perhaps somewhat fortuitous, but both theoretical results are remarkably close to our experimental value. Chadi and Chang [2] also calculated the atomic structure of As_{Ga}^{+}, i.e., of the As antisite after the emission of the first A_1 electron, and found a smaller As-As bond length by 0.06 Å than for As_{Ga}^{0}. This relaxation is also in excellent agreement with our value of 0.05 Å.

The above quantitative agreement between theory and experiment makes a compelling argument for the association of $EL2$ with the As antisite; however, in the absence of theoretical calculations for competing models and in view of the relatively large error bars on the values of the deformation potentials, it is imprudent to rule out other models. Nevertheless, it can be concluded that the present results are consistent with this association. We believe that these results will provide a stringent test for the ultimate resolution of the atomic structure of $EL2$.

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[13] Recent theoretical and semiempirical determinations of a_c have yielded the following values (in eV per unit volume strain): −7.3, −9.3, −7.7, −8.8, −8.5, and −10. (See Ref. [11] for all references to this footnote.) In view of the spread in these values, a_c can be alternately evaluated from the very accurately known hydrostatic pressure dependence of the band gap, $E_g = E_c - E_v$, of GaAs and the absolute pressure dependence of the valence band edge E_v. The most accurate value of dE_g/dP appears to be 10.73 ± 0.05 meV/kbar. As for the absolute pressure dependence of E_v, theoretical studies agree that the effect, or the deformation potential a_v $(-\partial E_v/\partial \ln V)$, is much smaller than a_c. Recent values for a_v (in eV) are −1.6, −0.1, 1.1, −1.0, and −0.7. We take the average of these values, -0.5 ± 1.0 eV, to be a representative value, which yields $dE_v/dP = 0.6 \pm 1.0$ meV/kbar. Combining this latter derivative with the above value for dE_g/dP yields $dE_c/dP = 11.3 \pm 1.0$ meV/kbar which corresponds to $a_c = -8.9 \pm 1.0$ eV. This value of a_c is compatible with the above cited values, agrees well with the value -9.3 ± 1.0 eV of Nolte, Walukiewicz, and Haller [14], and places realistic bounds on the magnitude of this important parameter. Any reasonable deviations from the above chosen values of a_c and a_v will not materially change the main conclusions of the paper.

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