Lawrence Berkeley National Laboratory
Recent Work

Title

ABSOLUTE PRESSURE DERIVATIVES OF DEEP LEVEL DEFECTS IN III-V SEMICONDUCTORS

Permalink

https://escholarship.org/uc/item/0bc3x7cb

Authors

Nolte, D.D.
Walukiewicz, W.
Haller, E.E.

Publication Date

1987-11-01

LBL-23599

Center for Advanced Materials

CAM

Presented at the 1987 Fall Meeting of the
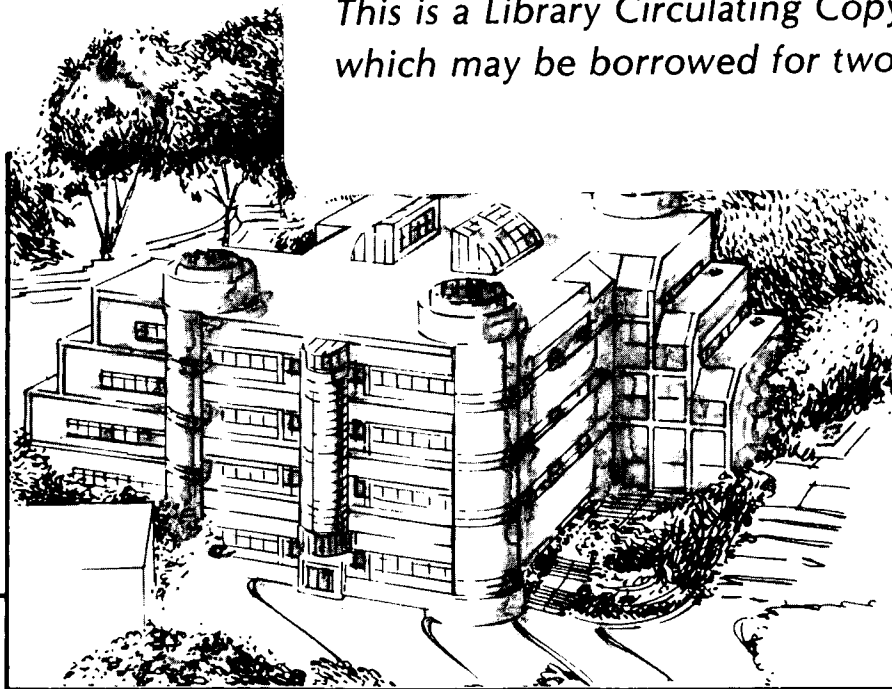Materials Research Society, Boston, MA,
November 30–December 4, 1987

**Absolute Pressure Derivatives of Deep Level
Defects in III-V Semiconductors**

D.D. Nolte, W. Walukiewicz, and E.E. Haller

November 1987

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

DISCLAIMER

ABSOLUTE PRESSURE DERIVATIVES OF DEEP LEVEL DEFECTS IN III-V SEMICONDUCTORS

D. D. Nolte, W. Walukiewicz and E. E. Haller
Center for Advanced Materials Lawrence Berkeley Laboratory and
University of California, Berkeley, 94720

ABSTRACT

Based on transition metal reference levels, we present absolute pressure derivatives for band-edges in GaAs and InP and defects in GaAs. The defect deformation potentials are directly related to the electron-lattice coupling which drives lattice relaxation around the defects. We find an exceedingly large inward lattice relaxation of the EL2 defect in GaAs upon electron emission.

DEFECT-LATTICE COUPLING

Many deep level defects in III-V semiconductors couple strongly to the lattice. This lattice-coupling drives the phenomena of large lattice relaxation which is the suspected cause of the metastable properties of such defects as EL2 in GaAs and the DX center in AlGaAs. The coupling of defect electronic energy to the lattice is defined by the electronic energy gradient; this gradient is the change in electronic energy per unit local lattice displacement around the defect. In practice, the coupling is measured by applying hydrostatic pressure to vary the lattice spacing. The lattice coupling, called the pressure derivative, is measured as the change in defect energy per unit stress. Photo- or thermal-ionization experiments performed under hydrostatic pressure probe differences between the lattice-couplings of initial and final states. However, these differences are obscured by the changes in the band-edge energies to which the carrier is emitted. The band-edge pressure changes are included in the experimental pressure derivatives. To extract the change in lattice-coupling of the defect upon carrier emission, this contribution from the band-edge must be subtracted away.

The problem of removing the effect of the energy change of the band-edge requires knowledge of the absolute pressure derivative of the band-edge. The measurement of absolute energies in turn requires a stable reference that remains invariant under the applied perturbation. Until recently, such a stable reference eluded definition. With the advent of band-gap engineering, however, the problem of predicting the band-edge discontinuity at a heterojunction interface created a special need for a reference level. In response to this need, several schemes for defining reference levels have been devised. Among them is one that uses transition metal defect energies as reference energies that line up across a hetero-

interface. We have extended this transition-metal-based energy reference to apply as well to absolute pressure derivatives. This extension is supported by substantial agreement with analyses of acoustic-phonon-limited mobility and with first principle calculations. With the new values for the band-edge pressure derivatives, the absolute pressure derivatives of deep level defects can be presented for the first time. The value for the defect-lattice coupling can further be used to derive the volume relaxation around the defects upon carrier emission.

TRANSITION METALS AS REFERENCE LEVELS

Transition metal defects in semiconductors are potential candidates for an absolute reference level because their energies are independent of composition. This independence of host properties was pointed out by early authors [1,2] and used by Langer[3] to predict band discontinuities at heterojunction interfaces. This idea is a conjecture which needs stringent experimental and theoretical proof. Experimental data on band discontinuities are scanty, but in the situation most studied (GaAs-AlAs) the transition-metal prediction is found to agree with the best available data. The prediction of the transition metal line-up also agrees with accurate first-principles calculations[4]. Such agreement could still be fortuitous. Before accepting the line-up of transition metal defects across hetero-interfaces as a general principle, a conceptual base must be found which can qualitatively explain the invariant nature of the transition metal defects.

The structure of substitutional transition metal defects have been studied in detail using Green's function calculations. The electronic structure can be qualitatively understood in terms of a three-level model[5]. In this model, the effect of the band structure on the defect energies can be represented by condensing the conduction and valence bands into single energy levels E_C^* and E_V^* which coincide with the maximum density of states of the conduction and valence bands respectively. The gap between these representative conduction and valence band energies is the dielectric gap, or Jone's Zone gap, of the semiconductor. This feature dominates the dielectric response of the semiconductor. The third energy of the three-level model is the transition metal d-electron energy, which changes as a function of chemical species. The transition metal level interacts with the two band energy levels, forming bonding, non-bonding, and anti-bonding combinations. The transition metal defect energy in the bandgap is the non-bonding combination.

Most of the semiemperical schemes for defining a reference level in the semiconductor rely on averages over the band structure. In these schemes, the reference level is defined by a mid-point energy between bonding and anti-bonding states. The correct band-edge line-up is found by lining up the mid-point energies between two semiconductors. This mid-point energy takes several forms, such as the center of the indirect gap[6], the dielectric-mean-energy at the center of the dielectric gap[7], or an inflection point in the crystal Green's function[8]. These semiemperical techniques agree within several tenths of an eV with each other, and with accurate first-principle calculations[4]. The non-bonding character of the transition metal defects connects them closely to the center of the Jone's Zone gap,

which remains invariant under perturbation of the semiconductor. Therefore, transition metal defects are expected to be locked to this internal reference level, and should provide a stable reference point from which to measure changes in band structure.

BAND-EDGE PRESSURE DERIVATIVES

The extension of the reference level to include the perturbation of applied stress is straightforward. Applied stress is a relatively mild perturbation of the band structure compared with changes in composition, and the reference level should be unaltered. Therefore, by measuring the pressure derivatives of the transition metals, one would in fact be measuring the band-edge deformation potential. This is again a conjecture which must be proven by comparison with independent experiment and theory. The first criterion that must be satisfied is that all transition metal defects within a given material must possess a universal pressure derivative, independent of charge state or chemical species. The second criterion is that this pressure derivative must yield a band-edge deformation potential that is consistent with the best available deformation potentials from electron and hole mobility experiments.

We have measured the pressure derivatives in GaAs of Ti(3+/2+), V (3+/2+), Ti (4+/3+) and Ni (2+/1+) using uniaxial stress. The energy positions of these defects are indicated in Fig. 1. Shear contributions to the energy shifts are negligible compared to the hydrostatic contributions [9]. These three transition metal defects among the different charge states yield similar pressure derivatives of 116 meV/GPa with respect to the conduction band, and therefore satisfy the first criterion of a universal pressure derivative independent of chemical species and charge state. The measured pressure derivatives are included in Fig. 1. The origin of the Figure is taken as the average of the four transition metal pressure derivatives. The inclusion of the Ni data with the Ti and V data is a crucial test of the limits of validity of the transition-metal-referenced deformation potentials.

The band-edge deformation potential corresponding to the measured pressure derivative for the conduction band in GaAs is $a_c = -9$ eV $\pm$ 1 eV. By subtracting the bandgap deformation potential from this value we obtain the valence band deformation potential $a_v = -0.4$ eV $\pm$ 1 eV. We have demonstrated elsewhere[10] that these values agree with the best measurements from acoustic-phonon-limited mobility in high purity GaAs. Similar stress experiments performed on the mid-gap Ti donor in InP yield $a_c = -7$ eV $\pm$ 1 eV and $a_v = -0.7$ eV $\pm$ 1 eV. These values are also in good agreement with accurate first principles calculations[10]. This agreement between our value (measured from the transition metals) and independent mobility and theoretical values for the band-edge deformation potentials satisfies the second criterion for the transition metals to provide a valid reference level. Supported by this weight of experimental and theoretical evidence, we claim that the transition metal defect pressure derivatives do in fact yield the correct band-edge deformation potentials. This principle is general, and should be applicable to any semiconductor. This should greatly facilitate the measurement of deformation potentials in materials that are not
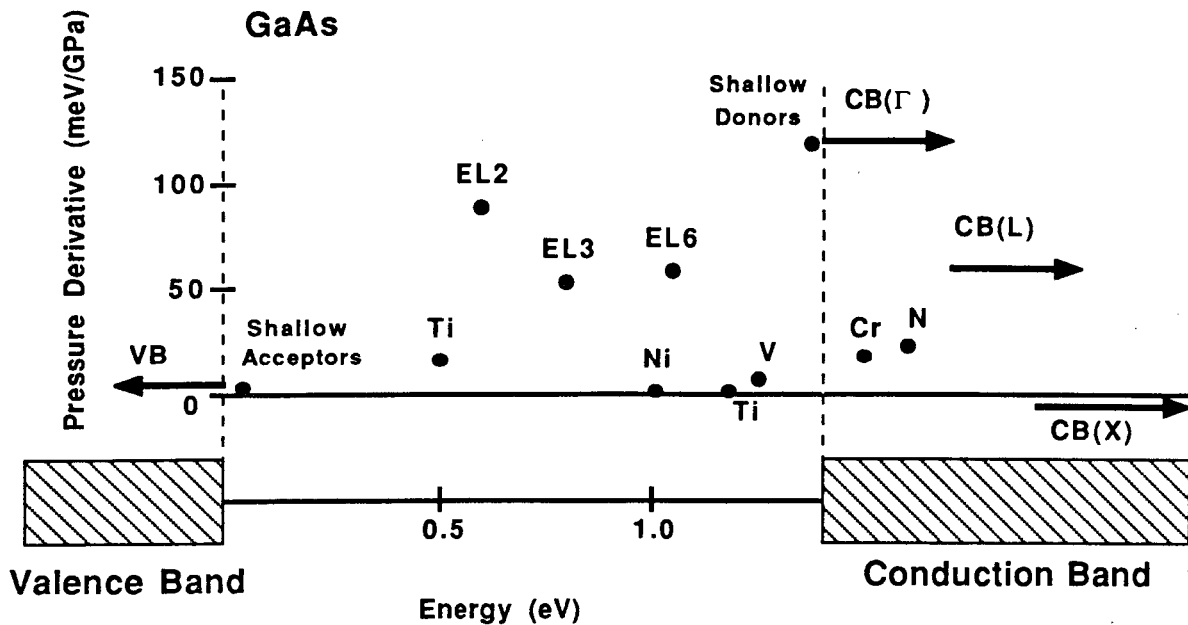
Fig. 1 Absolute pressure derivatives in GaAs. The origin is defined by the Ni(Ec - 0.39) and Ti (Ec - 0.24) pressure derivatives. The band-edge pressure derivatives are denoted by thick, horizontal lines. Also included are values for grown-in defects. All errors are approximately ± 20 meV/GPa. The data were obtained from: Ref[9] and Ref[11]; Bastide, Rev. Phys. Appl. 15, 1517(1980); Wolford, Proc. 17th ICPS, pg. 627; and Hennel, Phys. Rev. B25, 1039(1982)

available in sufficient purity to allow measurement of acoustic-phonon-limited mobility, such as in InP.

ISOTROPIC DEFECT-LATTICE COUPLING

From the band-edge pressure derivatives, the absolute pressure derivatives of deep level defects can be obtained from experimental pressure data. We present in Fig. 1 the absolute pressure derivatives of several defects in GaAs. The solid horizontal bars indicate the band-edge pressure derivatives, including the values for the indirect X and L conduction band minima. The zero is defined by the Ni and Ti transition metal pressure derivatives. The pressure derivative values presented for the defects are proportional to the change in the defect isotropic electron-lattice couplings upon emission of a carrier. Defects that produce energy levels resonant with the lowest conduction band minimum (Cr(2+/1+) and the N isoelectronic defect) likewise have similar pressure derivatives. The notable exceptions to the common pressure derivatives are the shallow level defects that are pinned to the band-edges, and the grown-in native defects[11]. The strong change in the isotropic coupling of EL2 may play a role in the metastable behavior of this technologically important defect.

Defect isotropic electron-lattice coupling describes how the electronic energy of a defect changes as the surrounding lattice sites move inwards or outwards isotropically. The gradient of this electronic energy with respect to the volume occupied by these lattice sites defines a pressure experienced by the surrounding atoms. The neighboring atoms relax in response to this pressure either inwards or outwards from the central defect site. The change in the isotropic electron-lattice coupling of defects upon carrier emission is therefore directly related to the change in lattice relaxation, or volume, upon carrier emission. Specifically, the defect absolute deformation potential Ξ is related to the volume change by

$$\Xi = B\,\Delta V + V\,\Delta B \qquad\qquad (1)$$

where V is the defect volume (approximately 62 Å^3 in a sphere with 2.45 Å radius), ΔV is the change in volume on carrier emission, B is the bulk modulus of the semiconductor, and ΔB is the change in the local bulk modulus around the defect upon carrier emission.

Contributions from the change in the local force constants (the second term on the right of the above equation) have been measured in Si to contribute only several hundred meV to the defect deformation potential[12]. On the other hand, the deformation potential of EL2 is $\Xi = 6.7$ eV. Therefore, if we neglect changes in the local force constants, then the change in the defect volume upon carrier emission can be approximated by the absolute defect deformation potential divided by the bulk modulus. This yields for EL2 an extraordinarily large inward volume relaxation of around 23% upon electron emission.

CONCLUSIONS

We have demonstrated that 3-d transition metal defects possess a universal pressure derivative in GaAs. Furthermore, we have presented strong evidence that the pressure derivative measured with respect to the conduction band is in fact the pressure derivative of the conduction band edge. Having determined the effect of changes in band-edge energy under pressure, the absolute pressure derivatives of deep level defects were derived. These pressure derivatives, in turn, can be used to estimate the change in lattice relaxation around the defect upon carrier emission. In particular, the defect EL2 in GaAs is found to have an exceedingly large isotropic relaxation inward upon electron emission.

References:

[1] L. Ledebo and B. K. Ridely, J. Phys. C15, L961(1982)

[2] M. J. Caldas, A. Fazzio and A. Zunger, Appl. Phys. Lett. 45, 671(1984)

[3] J. M. Langer and H. Heinrich, Phys. Rev. Lett. 55, 1414(1985)

[4] C. G. Van de Walle and R. M Martin, Phys. Rev. B35, 8154(1987)

[5] A. Zunger, Solid State Physics, vol. 39, Academic Press (1986)

[6] J. Tersoff, Phys. Rev. B32, 6968(1985)

[7] M. Cardona and N. E. Christensen, Phys. Rev. B35, 6182(1987)

[8] J. Tersoff, Phys. Rev. B30, 4874(1984)

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

[10] C. G. Van de Walle and R. M. Martin, unpublished

[11] D. D. Nolte, W. Walukiewicz and E. E. Haller, accepted Phys. Rev. B 36 (1987)

[12] G. A. Samara, Phys. Rev. B36, 4841(1987)