Native point defects in $Ga_xAl_{1-x}As_yP_{1-y}$

Eliza S. Ho and John D. Dow
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801
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The dependence on alloy composition x and y of the deep levels associated with vacancies and with antisite defects in the quaternary alloy $Ga_xAl_{1-x}As_yP_{1-y}$ is predicted.

The simplest native defects in III-V semiconductors are the anion and cation vacancies and the antisite defects: a cation on an anion site or an anion on a cation site.[1] In spite of the simplicity of these defects, none of their deep energy levels has been unambiguously identified in any semicondutor, although arguments have been set forth assigning various levels to specific defects.[2–4] The controversial nature of the level assignments suggests that it would be useful to know how the levels associated with each of these defects are expected to change with alloying. The purpose of this paper is to present such predictions.

We predict the deep levels of the native substitional defects in the quaternary alloy $Ga_xAl_{1-x}As_yP_{1-y}$ using a modification of the theory by Hjalmarson *et al.*[5] (The vacancy and antisite levels in the binary compounds have been predicted previously.[5]) This theory is based on a nearest-neighbor, tight-binding sp^3s^* Hamiltonian whose matrix elements exhibit manifest chemical trends[6]: Diagonal matrix elements are related to atomic energies and off-diagonal matrix elements are approximately inversely proportional to the square of the lattice constants. As in previous studies of vacancies and antisite defects in quaternary alloys,[7,8] the dominant effects of alloying can be accounted for in the virtual-crystal approximation, because the differences in diagonal matrix elements of the Hamiltonian for any two III-V compounds are considerably smaller in magnitude than the nearest-neighbor transfer-matrix elements.[9,10] Details of the calculational approach, which employs the Green's-function method,[11] have been published.[5,7,8]

The deep defect levels derived from the sp^3 manifold of basis states have A_1 (s-like) and T_2 (p-like) symmetry, because the virtual-crystal environment has tetrahedral (T_d) symmetry. Deviations from this (artifical) symmetry are expected to produce

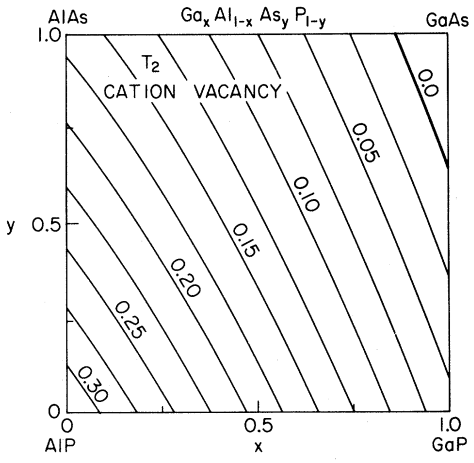

FIG. 1. Predicted contours of constant energy (in eV) of the deep T_2-symmetric level associated with cation vacancy of $Ga_xAl_{1-x}As_yP_{1-y}$, as functions of the alloy compositions x and y. The zero of energy is the valence-band maximum for all x and y. The heavy line labeled 0.0 corresponds to the alloy compositions for which this vacancy level is predicted to coincide with the valence-band maximum. The predictions for the binary compounds AlAs, AlP, GaAs, and GaP are the same as those previously obtained by Hjalmarson *et al.* (Ref. 5).

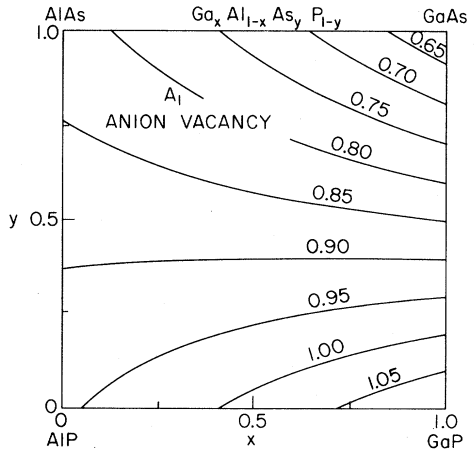

FIG. 2. Predicted contours of constant energy (in eV) of a A_1-symmetric level produced by an anion vacancy of $Ga_xAl_{1-x}As_yP_{1-y}$, as in Fig. 1.

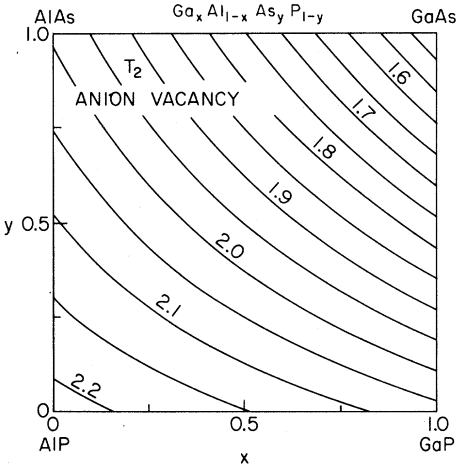

FIG. 3. Predicted contours of constant energy (in eV) of the T_2-symmetic level produced by an anion vacancy of $Ga_xAl_{1-x}As_yP_{1-y}$, as in Fig. 1.

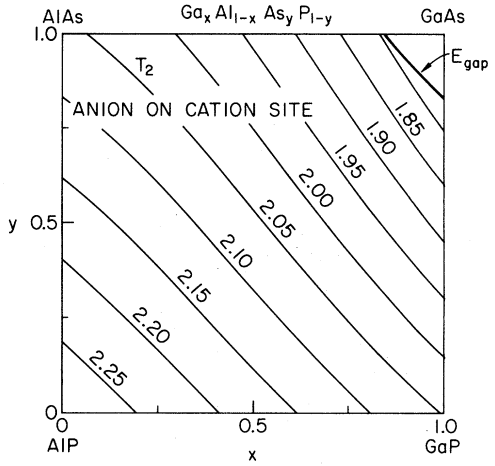

FIG. 5. Predicted contours of constant energy (in eV) of a T_2-symmetric level produced by an anion on the cation site of $Ga_xAl_{1-x}As_yP_{1-y}$, as in Fig. 1. The heavy line labeled E_{gap} corresponds to the predicted locus of alloy compositions for which the antisite-defect level coincides with the conduction-band edge.

only a slight alloy broadening, which is observed.[12] The contours of constant energy for the vacancies and the antisite defects in $Ga_xAl_{1-x}As_yP_{1-y}$ are given in Figs. 1—6. (The A_1-symmetric states associated with cation vacancies and cation on anion site defects are not predicted to yield levels in the gap.) The zero of energy in all cases is the valence-band maximum. The levels presented here for the compounds GaAs, GaP, AlAs, and AlP are the same as those reported previously by Hjalmarson *et al.*[5] The contour plots are quite different for the different defects and symmetries, indicating that the dependence on alloy composition (x and y) can be used to determine the site and the symmetry of the defect, and possibly even to distinguish between an antisite defect and a vacancy at the same site.

The theory is designed to properly account for the global chemical trends in the deep-level data, and therefore the general alloy dependences should be reliably predicted. The predicted energies of a specific defect may be in error by a few tenths of an electron volt however, because lattice relaxation, charge-state splittings, and electron-electron interactions have been omitted from the theory. These effects are often monotonic functions of the trap depth, as discussed previously.[5]

The absolute energy levels predicted are consistent

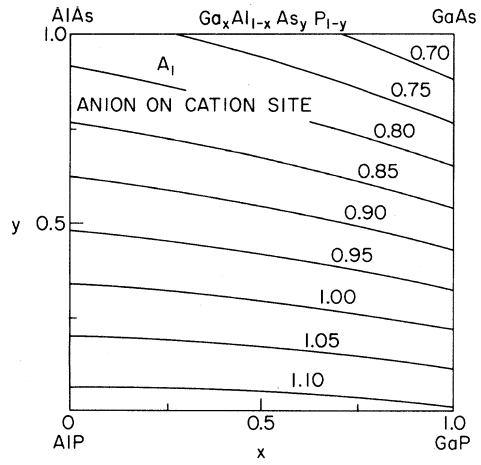

FIG. 4. Predicted contours of constant energy (in eV) of the deep A_1-symmetric level associated with an anion on the cation site of $Ga_xAl_{1-x}As_yP_{1-y}$, as in Fig. 1.

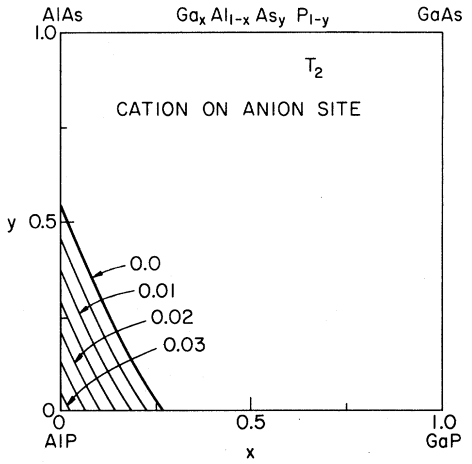

FIG. 6. Predicted contours of constant energy (in eV) of the T_2-symmetric level produced by a cation on the anion site of $Ga_xAl_{1-x}As_yP_{1-y}$, as in Fig. 1. The heavy line labeled 0.0 corresponds to the alloy compositions for which this antisite-defect level coincides with the valence-band maximum.

with the available experimental evidence concerning antisite defects in these materials,[4] but they disagree with some other theories.[13,14] For example, the level EL2 lying 0.7 eV above the valence band in GaAs has been assigned to an anion on cation site defect; the theory places this level at 0.6 eV,[15] which is very close to where it is observed.[4] There has been considerable controversy concerning the identification of EL2, however.[3,16,17] Most other data concerning III-V antisites have been gleaned from magnetic resonance data[18] and do not provide energy levels for comparison with the theory.

The vacancy levels are the "pinning" levels of the theory[5] and must be generally correct for the theory to have been so sucessful in describing many deep levels in compound semiconductors. We are aware of only one experimental result which appears to conflict with the theoretical predictions for vacancy levels: Kennedy and Wilsey,[19] in experiments whose interpretation has been controversial,[20] report that the A_1 level of the cation vacancy in GaP lies above this T_2 level, whereas most theories, including the present one,[5] predict the opposite ordering. Nevertheless, we expect the global chemical trends for the A_1 and T_2 vacancy levels, as functions of alloy compositions x and y, to be independent of the A_1-T_2 splitting and to be correctly predicted by the model.

Direct evidence that the predicted vacancy levels are in quantitive accord with the data comes from the 1.40-eV E2 level in GaAs, which has been assigned to an As vacancy[3] and is predicted to lie at 1.46 eV. Of course, a great deal of indirect evidence also supports the vacancy prediction, in that theoretically the energy levels of all the sp^3-bonded substitutional impurities in III-V semiconductors are "pinned" to and determined by vacancy levels.[5,21] If the predicted vacancy levels had been seriously in error, the model would not have successfully predicted the energy levels of so many defects and surface states.[21–23] We hope that the predicted dependences on alloy composition will be helpful for identifying the energy levels of native defects in $Ga_xAl_{1-x}As_yP_{1-y}$. Finally we call the reader's attention to the very recent and independent research of Lin-Chung and Reinecke[24] on antisite defect levels, which we have just received, and which is complementary to the present work.

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