Effect of alloy disorder on the deep levels produced by the anion vacancy in GaAs$_{1-x}$P$_x$

Sui-An Tang and Charles W. Myles

Department of Physics and Engineering Physics, Texas Tech University, Lubbock, Texas 79409-1051

William C. Ford, Jr.

McDonnell Douglas Electronic Systems Company, P.O. Box 516, St. Louis, Missouri 63166-0516

The inhomogeneous alloy broadening of the deep electronic levels produced by the ideal anion (As or P) vacancy in GaAs$_{1-x}$P$_x$ is calculated using an extension of previous work to the case of vacancy-associated levels broadened by second-neighbor disorder. Results are presented for the composition dependences of the spectra produced by the s-like and p-like vacancy-associated levels.

I. INTRODUCTION

In previous work,[1-3] we have presented a microscopic theory of the effects of alloy disorder on the deep levels associated with point defects in semiconductor alloys. These articles addressed the problems of the inhomogeneous alloy broadening of the deep levels produced by impurities[1] and vacancies[2] which occupy the ordered sublattice, where the alloy disorder nearest to the defect is in the first-neighbor shell of atoms surrounding it, and by impurities which occupy the disordered sublattice,[3] where the nearest alloy disorder is in the second-neighbor shell. This theory realistically accounts for local chemical environment effects, uses a deep-level theory[4] which has been shown to accurately predict chemical trends, and utilizes well-tested band structures for the alloy constituents.[5] In this Brief Report, we extend this theory to treat the deep levels associated with a vacancy on the disordered sublattice, and apply it to the investigation of the alloy broadening of the deep levels produced by the ideal anion (As or P) vacancy in GaAs$_{1-x}$P$_x$. The present work is thus an extension of the theory developed for the second-neighbor disorder problem, discussed in Ref. 3, to the case of vacancy-associated levels. Our primary interest, as in previous work, is in obtaining estimates of the size of the alloy broadening and in predicting trends as a function of x.

The alloy broadening of deep levels in semiconductor alloys occurs because different defects of the same type can be surrounded by different local configurations of alloy constituents. Since the deep-level properties of a defect are controlled primarily by its local environment,[4] each distinct configuration can produce a different deep level. The result is an inhomogeneously broadened deep-level spectrum associated with the defect. Several workers have observed these effects in optical absorption and luminescence from excitons bound to impurities in several semiconductor alloys.[6]

To our knowledge, such effects have not been observed for vacancy-associated levels. An estimate of the size of the alloy broadening of such levels might therefore be useful as a guide in the interpretation of data on such levels. The present treatment of the deep levels associated

with a vacancy with ordered first neighbors and disordered second neighbors is also a natural extension of the theory discussed in Ref. 2, where a vacancy with disordered first neighbors was treated. Further, a comparison of the widths of the inhomogeneously broadened spectra in the two cases will provide a complete qualitative picture of the alloy broadening of deep levels produced by vacancies in ternary semiconductor alloys. We have chosen the anion (P or As) vacancy in GaAs$_{1-x}$P$_x$ for study because of the technological importance of this material and in order to compare this case with that of the anion (As) vacancy in Al$_x$Ga$_{1-x}$As, which was treated in Ref. 2.

II. THEORY

The details of our theory have been presented in previous work.[1-3] Thus, we give only a brief discussion here. Our approach is based on the Hjalmarson et al.[4] theory and on the embedded-cluster method.[7,8]

The average properties of the alloy are described using the nearest-neighbor sp^3s^* tightbinding band structures of Vogl et al.[5] in the virtual-crystal approximation (VCA).[9] The sp^3s^* band structures[5] have proven accurate and useful in numerous studies of the defect properties of semiconductors.[10] The use of the VCA to describe the global alloy properties, rather than the coherent-potential approximation (CPA),[9] is justified by CPA calculations for GaAs$_{1-x}$P$_x$, which show that the CPA introduces only small corrections to the VCA.[11]

The local properties of the alloy are described using the embedded-cluster method.[7,8] Here we treat only the problem of a vacancy occupying a site on the disordered sublattice and we account only for the alloy disorder in the second-neighbor shell of atoms surrounding the vacancy site; the effects of higher neighbor disorder are neglected. To simulate this, following Ref. 3, a 17-atom cluster, consisting of a central anion (P or As) surrounded by four, ordered nearest-neighbor cations (Ga) and by a particular configuration of 12 disordered second-neighbor anions (P or As) is embedded in the VCA medium. The central atom of the cluster is replaced by a vacancy and its deep levels are calculated using the Hjalmarson et al.[4]

theory. This procedure is carried out for each cluster configuration and the contribution of each cluster's deep level to the spectrum is weighted by the probability of occurrence of that configuration. Following Ref. 3, we make the approximation that there are only 13 distinct configurations for the 12-atom second-neighbor shell, rather than attempt to treat the 4096 possible configurations which actually exist.[3] The 13 configurations we use are listed in Table I of Ref. 3.

In computing the vacancy-associated levels of the alloy, we make the ideal-vacancy approximation,[10,12,13] in which the diagonal matrix elements of the vacancy defect potential are taken to be infinite and the off-diagonal matrix elements are set to zero. This theory thus neglects lattice relaxation, which is certainly expected to be important in the case of a vacancy. It also neglects the charge-state splittings which result because different charge states of a vacancy can produce different deep levels; one can thus only treat a neutral vacancy in this manner. Use of this approximation and the related neglect of both lattice relaxation and charge-state splittings was justified in previous work,[10,13] where it was argued that such effects do not appreciably affect the chem-

ical trends in the vacancy-associated levels. Since we are interested in investigating the trends in the x dependence of the alloy broadening of the anion-vacancy-produced deep levels in $GaAs_{1-x}P_x$, this should be a reasonable first approximation. However, such effects should be included before any meaningful comparison between theory and experiment is attempted.

All of the calculations are carried out using a Green's function formalism. For the ideal vacancy, the deep-level energies E in the Hjalmarson et al.[4] theory are solutions to

$$\det[G(E)] = 0 . \tag{1}$$

In our case, $G(E)$ is the cluster Green's function, obtained via the embedded-cluster method for a particular configuration of the 17-atom cluster. In general, one expects different deep levels for each distinct configuration. Equation (1) only needs to be solved in the subspace of the ideal vacancy, so that it reduces to a 4×4 determinant in the tight-binding basis (for the four orbitals at the vacancy site). There are thus four solutions to Eq. (1), corresponding to the s-like level and the triply degenerate p-like level.
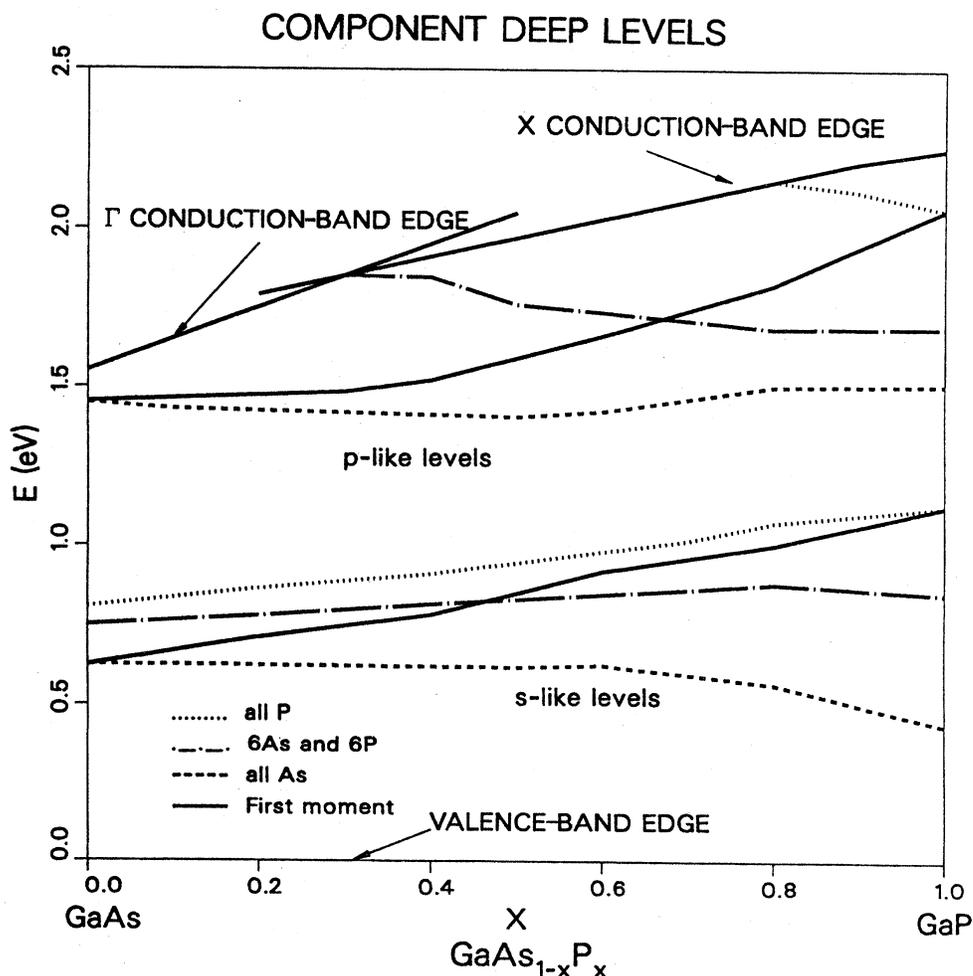

FIG. 1. Composition dependences of the component levels and the average energies for the alloy-broadened deep-level spectra produced by the ideal anion (P or As) vacancy in $GaAs_{1-x}P_x$ for the s-like and p-like vacancy-associated states.

For fixed x, Eq. (1) is solved for each cluster configuration. This results in s-like and p-like vacancy-induced deep-level spectra in the band gap of $GaAs_{1-x}P_x$. These spectra are a series of δ-function lines, one for each configuration. In these spectra, each line is weighted by the probability of occurrence of the configuration which produced it. We have used the binomial distribution for this purpose,[1−3] and have thus assumed that the alloy is completely random. This assumption is consistent with our previous work and could be straightforwardly modified to treat nonrandom alloys. The s- and p-like spectra can be characterized by their configuration averaged moments. Of particular interest are the x dependences of the average energies and the widths. The latter are a measure of the strength of the alloy broadening. The relationship of these moments to experimentally measured spectra can be subtle, however.[3]

III. RESULTS AND DISCUSSION

The results for the s-like and p-like alloy-broadened deep-level spectra of the ideal anion vacancy in $GaAs_{1-x}P_x$ are summarized in Figs. 1 and 2.

In Fig. 1, we show the x dependences of the component levels for three of the 13 cluster configurations treated. The ten other levels which exist in our approximation are interspersed between those shown. The levels shown correspond to the configurations consisting of all As atoms, six As and six P atoms, and all P atoms. Also shown are the composition dependences of the average energies of these spectra. As is clear from the figure, the s-like spectrum lies closer to the valence-band edge than the p-like spectrum. From the figure, it can be seen that all of the component levels are independent of the band edges as x is varied, in agreement with the expected behavior of deep levels.[4] Furthermore, they are not equally spaced, unlike the results of calculations of similar levels made using perturbation theory.[14] This effect is attributable to differences in the off-diagonal matrix elements of the sp^3s^* Hamiltonians for GaP and GaAs.

The behavior of the first moments as a function of x may be understood by considering the behavior of the component levels. For example, for the p-like spectrum, as the different component deep levels exit the band gap
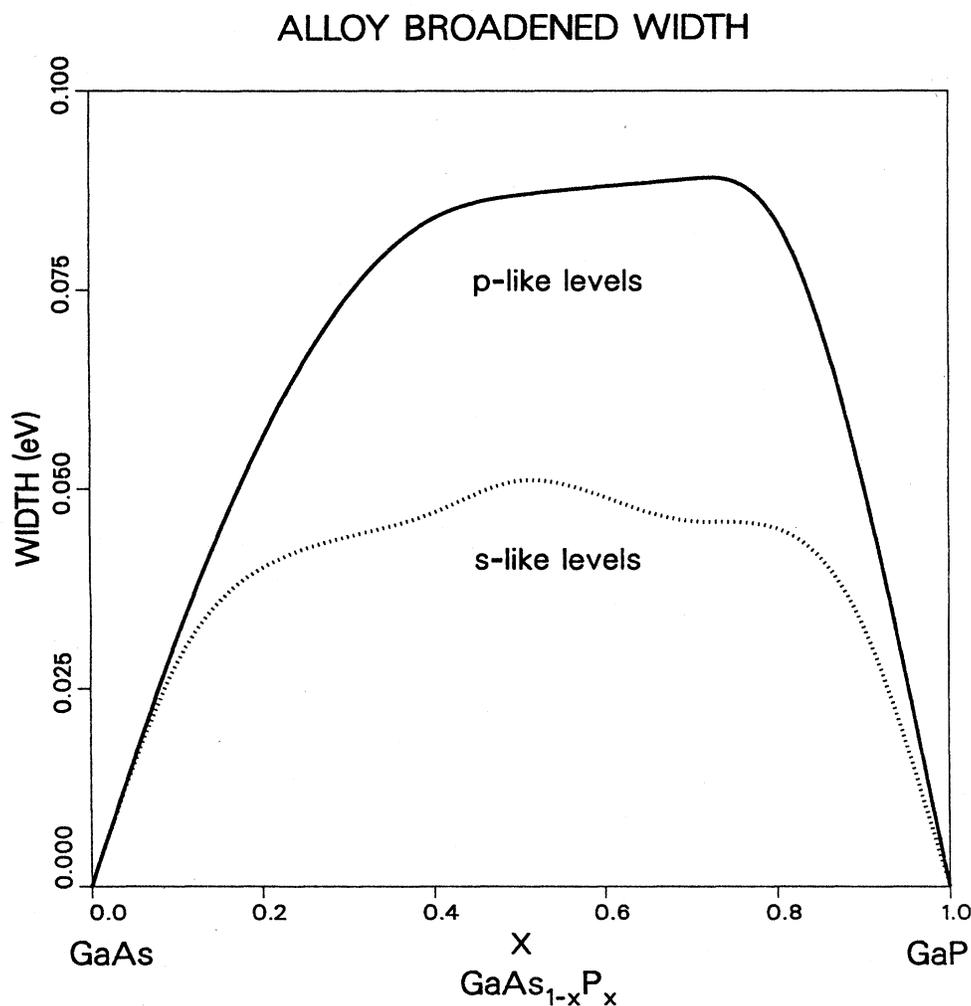
ALLOY BROADENED WIDTH

FIG. 2. Composition dependences of the widths of the alloy-broadened deep-level spectra produced by the ideal anion (P or As) vacancy in $GaAs_{1-x}P_x$ for the s-like (dashed curve) and p-like (solid curve) vacancy-associated states.

(as x decreases) and become conduction-band resonant, the first moment is displaced deeper into the band gap due to the fact that band-resonant levels no longer contribute. Such levels have been given zero weight in the δ-function spectrum, following earlier work.[1-3] Except at compositions where a component level becomes band resonant, the first moment follows the VCA deep-level energy predicted by Ho and Dow,[13] to within the accuracy of the sp^3s^* parameters. Finally, the A_1 (s-like) and T_2 (p-like) levels for the ideal anion vacancies in GaP and GaAs, obtained earlier by Hjalmarson et al.,[4] are reproduced by the first moments of Fig. 1 at $x=1$ and $x=0$, respectively.

Figure 2 illustrates the spectrum widths as functions of x for the s-like and p-like spectra. The dashed curve is the width of the s-like spectrum, while the solid curve is the width for the p-like states. All of the component levels of the s-like spectrum lie in the band gap for all x. Thus, they all contribute to the spectrum for all compositions. This gives rise to a relatively smooth width versus x curve, that nonetheless displays a slight asymmetry about $x=0.5$. By contrast, as x decreases from unity, some of the component levels of the p-like spectrum exit the band gap and become conduction-band resonant. Thus, the width versus x curve in this case has an even greater asymmetry about $x=0.5$.

More important than the shape of the width versus x curves are their magnitudes, which are estimates of the importance of the alloy broadening of vacancy-associated levels in $GaAs_{1-x}P_x$. For the s-like spectrum, this width is predicted to be of the order of 30–50 meV for most x, while for the p-like spectrum, a width of 30–90 meV is predicted. These widths are of comparable sizes to the analogous widths predicted for the ideal anion vacancy in $Al_xGa_{1-x}As$.[2] Thus, the magnitude of the alloy broadening is predicted to be similar in the two cases. This may seem surprising at first glance, since the calculations of Ref. 2 have treated first-neighbor alloy disorder, while the present calculations have treated second-neighbor disorder. However, the alloys in the two cases are different, so that a direct comparison is difficult to make. It is clear from the present calculations, however, that the inhomogeneous broadening of the anion-vacancy-associated levels in $GaAs_{1-x}P_x$ is certainly large enough to be observable, and could be an important effect for understanding such levels in this material.

ACKNOWLEDGMENTS

[1] C. W. Myles and W. C. Ford, J. Vac. Sci. Technol. A **4**, 2195 (1986); W. C. Ford and C. W. Myles, Phys. Rev. B **34**, 927 (1986); W. C. Ford, Ph.D. dissertation, Texas Tech University, 1986.

[2] W. C. Ford and C. W. Myles, Phys. Rev. B **38**, 1210 (1988).

[3] W. C. Ford, C. W. Myles, and R. L. Lichti, Phys. Rev. B **38**, 10 533 (1988).

[4] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. **44**, 810 (1980).

[5] P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).

[6] D. J. Wolford, B. G. Sreeetman, and J. Thompson, J. Phys. Soc. Jpn. Suppl. A **49**, 223 (1980); J. H. Collet, J. A. Kash, D. J. Wolford, and J. Thompson, J. Phys. C **16**, 1283 (1983); L. Samuelson, S. Nelson, Z. G. Wang, and H. G. Grimmeiss, Phys. Rev. Lett. **53**, 150 (1984); J. A. Kash, Phys. Rev. B **29**, 7069 (1984); J. A. Kash, D. J. Wolford, and A. Marbeuf, ibid. **31**, 5217 (1985); J. A. Kash, H. Mariette, and D. J. Wolford, ibid. **32**, 3753 (1985).

[7] C. W. Myles and J. D. Dow, Phys. Rev. Lett. **42**, 254 (1979); Phys. Rev. B **19**, 4939 (1979); C. W. Myles, ibid. **28**, 4519 (1983); Y.-T. Shen and C. W. Myles, ibid. **30**, 3283 (1984); C. W. Myles, J. D. Dow, and O. F. Sankey, Phys. Rev. B **24**,

1137 (1981); C. W. Myles and J. D. Dow, ibid. **25**, 3593 (1982); W. C. Ford, C. W. Myles, and Y.-T. Shen, Phys. Rev. B **32**, 3416 (1985).

[8] A. Gonis and J. W. Garland, Phys. Rev. B **16**, 2424 (1977); A. Gonis, Phys. Rev. Lett. **53**, 1501 (1984).

[9] R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. **46**, 469 (1974).

[10] C. W. Myles, P. F. Williams, R. A. Chapman, and E. G. Bylander, J. Appl. Phys. **57**, 5279 (1985); C. W. Myles and O. F. Sankey, Phys. Rev. B **29**, 6810 (1984); O. F. Sankey and J. D. Dow, J. Appl. Phys. **52**, 5139 (1981); Phys. Rev. B **26**, 3243 (1982); Y.-T. Shen and C. W. Myles, J. Appl. Phys. **65**, 4273 (1989); Appl. Phys. Lett. **51**, 2304 (1987); Y.-T. Shen, Ph.D. dissertation, Texas Tech University, 1986.

[11] A. B. Chen and A. Sher, Phys. Rev. B **23**, 5360 (1981); Y.-T. Shen and C. W. Myles, J. Phys. Chem. Solids **48**, 1173 (1987). The second paper also utilized the band structures of Ref. 5.

[12] S. Das Sarma and A. Madhukar, Phys. Rev. B **24**, 2051 (1981); J. Bernholc and S. T. Pantelides, ibid. **18**, 1780 (1978).

[13] E. S. Ho and J. D. Dow, Phys. Rev. B **27**, 1115 (1983).

[14] C. W. Myles, S.-F. Ren, R. E. Allen, and S.-Y. Ren, Phys. Rev. B **35**, 9158 (1987).