PHYSICAL REVIEW B **71**, 155201 (2005)

Similar and dissimilar aspects of III-V semiconductors containing Bi versus N

Yong Zhang* and A. Mascarenhas
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401, USA

L.-W. Wang
NERSC, Lawrence Berkeley National Laboratory, Berkeley, California 94720

(Received 17 August 2004; revised manuscript received 9 December 2004; published 6 April 2005)

We show through band structure calculations that III-V-Bi alloys, emerging as a new class of semiconductor materials, differ nontrivially from their counterparts III-V-N alloys which have been intensively studied in the past decade. For a prototype system, $GaAs_{1-x}Bi_x$ with a small amount of Bi, a large band gap reduction, due to the shift of the perturbed host band edges, resembles the effect of N incorporation in GaAs, but $GaAs_{1-x}Bi_x$ exhibits a number of striking differences from $GaAs_{1-x}N_x$: (1) Bi generates a resonant impurity state in the valence band as a strongly perturbed host state, while N produces a resonant impurity state additional to the host states in the conduction band; (2) Under pressure, the Bi impurity state sinks further into the valence band, while the N impurity state emerges as a bound state; (3) the spin-orbit splitting increases superlinearly with increasing Bi amount, while it decreases sublinearly with increasing N amount. Qualitative conclusions for III-V-Bi are generally applicable for other isoelectronic donors in semiconductors.

DOI: 10.1103/PhysRevB.71.155201 PACS number(s): 71.20.Nr, 71.15.Rf, 71.55.Eq

Recently, in an effort to expand the repertory of III-V and II-VI semiconductor alloys to meet the growing demand of new technologies, a great deal of effort has been devoted to explore nonconventional alloys. These alloys are typically obtained by incorporating either very light or very heavy elements, viewed as isoelectronic acceptors or donors,[1] into a traditional binary (e.g., N or Bi in GaAs and GaP, O in ZnTe, and Te in CdS). It is not only technologically very challenging to grow these materials, but also not trivial to comprehend the electronic structures of these nonconventional alloys. Intensive and extensive studies have been directed to understanding various peculiarities in the properties of III-V-N alloys, for instance, strong band gap tunability,[2–8] impurity states, impurity-host interaction and resonant optical transitions,[5–11] N solubility and related defect states,[12] and the effect of hydrogen.[13,14] However, much less can be found for their counterparts, III-V-Bi,[15,16] which to a large extent is due to the disparity in the development of N and Bi related materials. In fact, most III-N binary nitride semiconductors have been grown, but none of the III-Bi compounds is known to exist in reality with the exception of InBi,[15] which adds difficulty to modeling the III-V-Bi alloys using empirical methods,[7] since the empirical parameters for the end-point III-Bi compounds are not readily available.

For over 2 decades, III-V-Bi alloys have attracted interest for potential applications in the infrared spectral region, because of the belief that alloying conventional III-V semiconductors with the virtual semimetallic III-Bi compounds could lead to low band gap (E_g) materials like the anion alloys In(Sb or As or P)$_{1-x}$Bi$_x$ and the cation alloys (Ga or Al)$_{1-y}$In$_y$Bi or Al$_{1-y}$Ga$_x$Bi.[15] The activities in III-V-N have led to a renewed interest in III-V-Bi.[16–20] Physically, the similar and dissimilar aspects of the isoelectronic acceptor and donor and their related alloys are of quite general interest. Technologically, there is a potential advantage to use $GaAs_{1-x}Bi_x$ instead of $GaAs_{1-x}N_x$ for achieving the goal of tuning band gap, because incorporating Bi or N primarily distorts the valence band (VB) and conduction band (CB), respectively, and there is an intrinsic asymmetry between the carrier mobilities for electrons and holes. Recently, a reduction in the temperature coefficient of band edge emission has been reported for $GaAs_{1-x}Bi_x$ and $InAs_{1-x}Bi_x$, which is hoped to offer an improvement on device stability.[17,18] Another interesting subject related to Bi is codoping Bi and N into III-V binaries (e.g., GaAs and GaP),[16,19] because such codoping is expected to enhance the solubility of both N and Bi, to compensate the lattice mismatches of GaN and GaBi with respect to GaAs or GaP, and to offer greater tunability of the host band structure. Only very recently has incorporating Bi into bulk GaAs been demonstrated in a controllable manner in epitaxial growth, which has allowed a systematical study to be performed on a III-V-Bi alloy system.[20] Indeed, Bi incorporation in GaAs can result in a large band gap reduction (δE_g),[20] significantly exceeding the calculated value.[16] Toward the impurity limit, it is well known that in GaP, an isolated N or Bi introduces a bound state below the conduction band minimum (CBM) or above the valence band maximum (VBM).[21,22] And, in GaAs, the impurity state of an isolated N is resonant above CBM.[23] However, the location of the Bi impurity state in GaAs is unknown experimentally, although a bound state has been predicted at 180 meV above the VBM, based on a 64-atom cell calculation.[16] The existence of such a deep bound state would be rather surprising, given the fact that the Bi bound state lies only ~60 meV above the VBM in GaP,[22] which in fact is more favorable for Bi to have a bound state. Therefore, a better understanding of the behavior of Bi as an impurity in III-V semiconductors and the evolution of the electronic structure of III-V-Bi with increasing Bi doping level is critically needed for further exploring its potential for device applications.

In this paper, we present a systematical study on the electronic structure of a prototype III-V-Bi alloy, $GaAs_{1-x}Bi_x$, using a self-consistent pseudopotential-based charge-patching method.[24] We find that (1) the calculated δE_g agrees very well with experimental results; (2) Bi incorporation strongly enhances the spin-orbit splitting (E_{SO}); (3) the alloy VBM is derived from the host VBM rather than the Bi bound state; (4) Bi forms a resonant state below the VBM rather than a bound state; and (5) Bi impurity state has a smaller pressure coefficient than the band gap. Important and nontrivial differences between III-V-N and III-V-Bi are revealed and discussed.

An ordered array of Bi impurities embedded in GaAs is used to simulate the $\mathrm{GaAs}_{1-x}\mathrm{Bi}_x$ alloy. Specifically, we put one Bi atom in a supercell with size $n_1 \times n_2 \times n_3$ of the 8-atom primary cell, varying n_i from 2–8. We first calculate a 64-atom cell with one Bi at the center self-consistently with full atomic relaxation, using the first-principles plane-wave pseudopotential method within the local density approximation (LDA). The Ga 3*d* electrons are included as valence electrons. For a larger supercell, the charge density and atomic configurations of the 64-atom cell are patched onto the central portion of the supercell, and the surrounding portion remains the same as that of GaAs. E_{cut} in the plane-wave expansion is 60 Ry. More details about this technique and other considerations can be found in Ref. 24. Corrections to the nonlocal potentials of Ga and As atoms are introduced to empirically fix the LDA errors in band gaps at the Γ, L, and X points.[24] Such corrections affect not only the CB but also the VB and the Bi impurity state primarily derived from the VB, because of the *p-d* and *s-d* coupling. This procedure has been found to be very effective in our previous band structure calculations for $\mathrm{GaAs}_{1-x}\mathrm{N}_x$.[8,25] The lattice constant of the alloy is assumed to obey Vegard's rule, with the lattice constant of GaBi equal to 6.324 Å, calculated by the full-potential linearized augmented plane-wave (FLAPW) method.[16] Note that the use of the newly developed charge-patching method allows us to calculate sufficiently large systems, and to reveal the correct physics that has been obscured in the previous effort.[16]

First, in Fig. 1(a), we compare the calculated band gap reduction, $\delta E_g(x)$, with experimental data obtained from modulation spectroscopy.[20] Here, the calculated band gap is derived from the energy difference between the lowest unoccupied state and the highest occupied state. The origin of the occupied state will be examined later. The good agreement between our calculation and experiment over the entire experimentally studied composition range indicates the success of this method, and offers assurance for investigating other effects due to Bi doping. $\delta E_g(x)$ from the previous calculation[16] is found to be significantly smaller than the experimental value. The band gap reduction in $\mathrm{GaAs}_{1-x}\mathrm{Bi}_x$ is comparable to, though slightly smaller than, that in $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ for the same doping level,[8] and should be observable experimentally for x as low as 0.05%. Several effects contribute jointly to $\delta E_{\mathrm{g}}(x)$: the chemical difference between As and Bi, the lattice relaxation due to atomic size mismatch, the global lattice expansion due to Bi incorporation, and the enhancement in E_{SO}. The last effect is negligible for $\mathrm{GaAs}_{1-x}\mathrm{N}_x$.

The first important prediction of this calculation is that $E_{\mathrm{SO}}(x)$ in $\mathrm{GaAs}_{1-x}\mathrm{Bi}_x$ is strongly enhanced, as shown in Fig. 1(b), due to a very large spin-orbit splitting of 2.2 eV for GaBi associated with the large relativistic effect for the heavy element Bi. The enhancement is in fact superlinear and far exceeding the expectation of a linear interpolation, due to the strong localization of the hostlike VB states at Bi sites. δE_{SO} contributes to δE_{g} by a non-negligible amount, $\sim \delta E_{\mathrm{SO}}/3$. This is in contrast to the situation for $\mathrm{GaAs}_{1-x}\mathrm{N}_x$, where E_{SO} remains nearly constant for x up to a few percent,[5] due to a complementary effect, i.e., the antilocalization of the hostlike VB states at N sites.

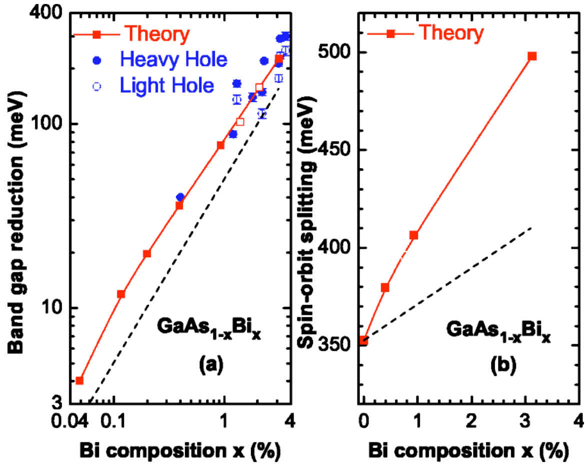

FIG. 1. (Color online) $\delta E_g(x)$ (a) and $E_{\mathrm{SO}}(x)$ (b) as a function of Bi composition. The blue symbols are experimental data, the red symbols (connected with red solid lines) are the results of this calculation. The dashed black lines are the calculated result of Ref. 16 in (a) and linear interpolation in (b).

The origin of the VBM in $\mathrm{GaAs}_{1-x}\mathrm{Bi}_x$ is critically important for device applications. Although in both GaAs and GaP the incorporation of N results in a large redshift of the absorption edge, the primary contributors to the absorption in the new band edge are in fact very different for these alloys, being hostlike states for GaAs but N impuritylike states in GaP,[25] due to the fact that an isolated N impurity does not produce a bound state in GaAs but does so in GaP.[21,23] In previous 64-atom cell calculation for $\mathrm{GaAs}_{1-x}\mathrm{Bi}_x$,[16] the VBM state was found to be localized at the Bi site, which led to the conclusion that the VBM state evolved from a Bi bound state. It should be pointed out that both the genuine Bi-impurity state and the perturbed host VBM state have the tendency to localize at the Bi site, just as for the case of $\mathrm{GaAs}_{1-x}\mathrm{N}_x$, where the charge density for both the perturbed CBM state and the resonant N-impurity state maximizes at the N site.[24] This tendency can be understood as being due to the fact that the 2*s* state of N is significantly lower than that of the 3*s* of P or 4*s* of As;[26] thus, N generates a potential trap for the electron either in the N-impurity state or the CBM state. Similarly, because the 6*p* state of Bi is substantially higher than that of the 3*p* of P or 4*p* of As, Bi is likely to generate a potential trap for the hole either in the Bi-impurity state or the VBM state. Comparing GaAs with GaP, one should notice that because 4*s*(As) is lower than 3*s*(P), a N bound state is less likely to form in GaAs than in GaP. Similarly, since 4*p*(As) is higher than 3*p*(P), a Bi bound state is less likely to form in GaAs. Therefore, it is difficult to judge

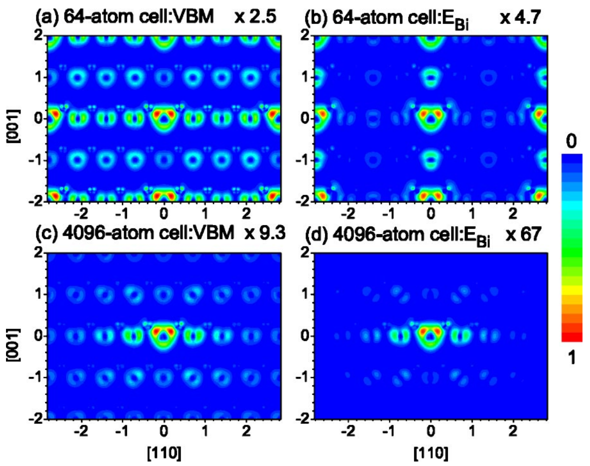

FIG. 2. (Color online) Charge density plots for the VBM and E_{Bi} states on the (110) plane for the 64-atom and 4096-atom supercells, in an area of $4\sqrt{2}\,a\times 4a$ (a is the lattice constant). For each map, the intensity is normalized, with the enhancement factor relative to that of GaAs given on the subtitle line.

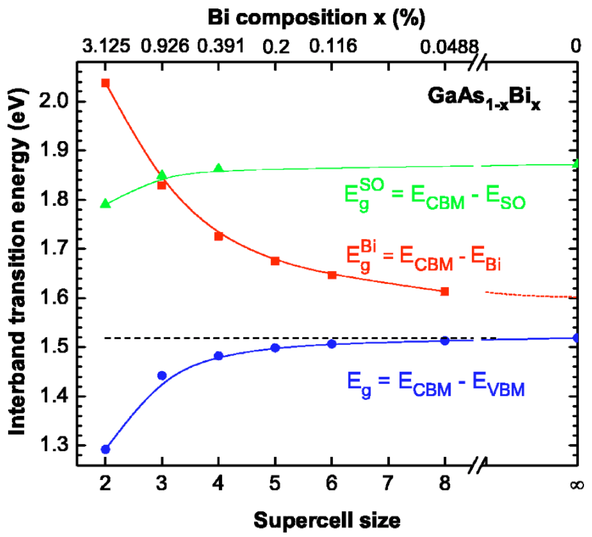

FIG. 3. (Color online) Interband transition energies for E_g(blue), E_g^{Bi}(red), and E_g^{SO}(green) as a function of supercell size.

whether or not a seemingly localized state is actually derived from a bound state in the dilute doping limit just by looking at the wave function from small cell calculations, and the exact origin of the VBM state can only be determined by examining the evolution of this state by varying (reducing) the doping level. Figures 2(a) and 2(c) show the charge distribution in the (110) plane for the VBM state with two supercell sizes. The intensity maximizes at the Bi site, but is also present at all As sites, which renders a perturbed charge distribution of the GaAs VBM. In fact, with increasing supercell size, although there is always an enhanced peak at the Bi site, by borrowing the charge from the volume away from the Bi site, the intensity at As sites asymptotically approaches that of GaAs when moving away from the center. This situation is in fact very similar to that in GaAs:N.[24] Also, the energy of the VBM clearly converges to that of the GaAs VBM, as shown in Fig. 3 (for the 4096-atom cell, the difference is mearly 7.5 meV). Thus, we conclude that the VBM state of GaAs$_{1-x}$Bi$_x$ is derived from that of GaAs rather than a Bi bound state, and Bi does not form a bound state in GaAs!

This raises the question, where is the Bi impurity state, if any? For the case of GaAs:N, N actually introduces a resonant impurity state in addition to the host states near the CBM, which leaves no ambiguity about the existence of such an impurity state. For the case of GaAs:Bi, if it remains as a semiconductor the expected Bi impurity state, whether located below or above the VBM, has to be occupied. This means that the formation of an impurity state occurs at the cost of a host state in the VB. There will be no ambiguity in identifying the impurity state, if it is a real bound state, as for the cases of GaP:Bi, InP:Bi, and other isoelectronic donors.[27] In the supercell approach, such a bound state is found to converge energetically to a level above the bulk VBM for a sufficiently large supercell, say, with 4096 atoms.[27] One may understand the formation of the bound states as a result of that the impurity potential pulls some states out of the VB. However, when no bound states exist, as in the current system, it becomes less trivial to infer a resonant state being the impurity state as opposed to being a bulklike folded state, in contrast to the case of GaAs:N. To identify the impurity state, we have performed the following analyses for the relevant states below the VBM: (1) Examine the charge distribution and the evolution with varying supercell size; (2) Project the wave function to a grid of k points that have been folded onto the Γ point; (3) Track the dependence of the energy level on supercell size. We have found that for any one of the supercell sizes ($n=2$–8), there is always one state, called E_{Bi} thereafter, whose wave function is composed of bulk states from different $\boldsymbol{k}$ points, but predominantly from $(1/n,\ 1/n,0)\ k_0$ along the Σ line $(1/n,1/n,1/n)k_0$ along the Λ line, $(1/n,0,0)k_0$ along the Δ line, and the Γ point. The charge distribution of E_{Bi} is found to be more strongly localized around the Bi site than that of the VBM state, as shown in Figs. 2(b) and 2(d). It in fact diminishes at As sites away from the impurity with increasing supercell size. E_{Bi} strongly depends on the Bi concentration. Without the spin-orbit interaction, it is a triplet state below the triplet VBM. With spin-orbit interaction included, E_{Bi} splits into a doublet and a singlet with the doublet lying above, just as for the VBM. In this calculation, we only track the doublet. The interband transition energies (E_g, $E_g^{\mathrm{Bi}}=E_{\mathrm{CBM}}-E_{\mathrm{Bi}}$, and $E_g^{\mathrm{SO}}=E_{\mathrm{CBM}}-E_{\mathrm{SO}}$) from the VBM, E_{Bi} and E_{SO} to the CBM are depicted in Fig. 3. Thus, the second important prediction is that E_{Bi} extrapolates to ~80 meV below the VBM of GaAs in the dilute doping limit (i.e., $n\rightarrow\infty$).

It is very interesting to note that the deformation potential for E_g^{Bi} is larger than that of E_g (e.g., -8.03 eV vs -7.81 eV for $x\rightarrow 0$ and -8.75 eV vs -7.84 eV for $x=3.125\%$), which implies that applying a hydrostatic pressure will not make E_{Bi} emerge from the VB, in stark contrast to the behavior of the N impurity state that drops into the band gap under pressure.[23] The seemingly opposite pressure dependence for Bi and N is in fact due to the same reason that the impurity state has a smaller absolute deformation potential (in magnitude) than that of the corresponding Γ point band edge state. It is worth pointing out that the expected pressure behavior of E_{Bi} in fact corroborates with a recent experimental finding that Te (an isoelectronic donor) bound state in ZnS:Te has a larger pressure coefficient than that of the band gap.[28]

We now discuss the significance of these results for further spectroscopy studies of the $\mathrm{GaAs}_{1\text{-}x}\mathrm{Bi}_x$ alloy. Note that on one hand, the behavior of E_{Bi} is similar to that of the resonant N impurity state in the CB of GaAs:N; on the other hand, since there is no state added to the VB, this state could be viewed as well as a strongly perturbed host state. For $\mathrm{GaAs}_{1-x}\mathrm{N}_x$, a legitimate task has been to determine whether an above band gap transition (often referred to as E_+) is related to the resonant N state[6,29] or to the L point,[9,11] which until today still remains controversial. The subtle difference between N and Bi should be kept in mind when analyzing optical transitions involving states above the band edge (e.g., modulation spectroscopy[5] and resonant Raman[29]). In addition, the strong x dependence for both $E_{\mathrm{Bi}}(x)$ and $E_{\mathrm{SO}}(x)$ is expected to introduce extra complexity in spectroscopy studies in the region above the band gap.

The qualitative conclusions of this study are expected to be valid for other III-V-Bi alloys as well as other semiconductors with similar type of isoelectronic doping, and should offer useful guidance for further experimental exploration of these systems.

ACKNOWLEDGMENTS

We thank S.-H. Wei for valuable discussions. This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-99GO10337 at NREL, DE-AC03-76SF00098 at LBNL. The resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy, were utilized.

---

*Email address: yong_zhang@nrel.gov

[1] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. **17**, 312 (1966).

[2] A. Rubio and M. L. Cohen, Phys. Rev. B **51**, 4343 (1995).

[3] J. Neugebauer and C. G. Vandewalle, Phys. Rev. B **51**, 10 568 (1995).

[4] S. H. Wei and A. Zunger, Phys. Rev. Lett. **76**, 664 (1996).

[5] J. D. Perkins, A. Mascarenhas, Y. Zhang, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 3312 (1999).

[6] W. Shan, W. Walukiewicz, J. W. Ager, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 1221 (1999).

[7] P. R. C. Kent and A. Zunger, Phys. Rev. Lett. **86**, 2613 (2001).

[8] Y. Zhang, B. Fluegel, M. C. Hanna, A. Mascarenhas, L. W. Wang, Y. J. Wang, and X. Wei, Phys. Rev. B **68**, 075210 (2003).

[9] N. G. Szwacki and P. Boguslawski, Phys. Rev. B **64**, 161201 (2001).

[10] L. W. Wang, Phys. Rev. Lett. **88**, 256402 (2002).

[11] S. Francoeur, M. J. Seong, M. C. Hanna, J. F. Geisz, A. Mascarenhas, H. P. Xin, and C. W. Tu, Phys. Rev. B **68**, 075207 (2003).

[12] S. B. Zhang and S. H. Wei, Phys. Rev. Lett. **86**, 1789 (2001).

[13] A. Janotti, S. B. Zhang, and S. H. Wei, Phys. Rev. Lett. **88**, 125506 (2002).

[14] A. Janotti, S. B. Zhang, S. H. Wei, and C. G. Van de Walle, Phys. Rev. Lett. **89**, 086403 (2002).

[15] M. A. Berding, A. Sher, A. B. Chen, and W. E. Miller, J. Appl. Phys. **63**, 107 (1988).

[16] A. Janotti, S. H. Wei, and S. B. Zhang, Phys. Rev. B **65**, 115203 (2002).

[17] K. Oe and H. Okamoto, Jpn. J. Appl. Phys., Part 2 **37**, L1283 (1998).

[18] H. Okamoto and K. Oe, Jpn. J. Appl. Phys., Part 1 **38**, 1022 (1999).

[19] A. Mascarenhas, Y. Zhang, J. Verley, and M. J. Seong, Superlattices Microstruct. **29**, 395 (2001).

[20] S. Francoeur, M. J. Seong, A. Mascarenhas, S. Tixier, M. Adamcyk, and T. Tiedje, Appl. Phys. Lett. **82**, 3874 (2003).

[21] D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966).

[22] F. A. Trumbore, M. Gershenzon, and D. G. Thomas, Appl. Phys. Lett. **9**, 4 (1969).

[23] D. J. Wolford, J. A. Bradley, K. Fry, J. Thompson, and H. E. King, in *Proceedings of the 17th International Conference on the Physics of Semiconductors*, edited by J. D. Chadi and W. A. Harrison (Springer, New York, 1984), p. 627.

[24] L. W. Wang, Appl. Phys. Lett. **78**, 1565 (2001).

[25] Y. Zhang, B. Fluegel, M. C. Hanna, J. F. Geisz, L.-W. Wang, and A. Mascarenhas, Phys. Status Solidi B **240**, 396 (2003).

[26] S. H. Wei and A. Zunger, Phys. Rev. B **60**, 5404 (1999).

[27] J. B. Li and L. W. Wang, Phys. Rev. B **67**, 033102 (2003).

[28] Z. L. Fang, F. H. Su, B. S. Ma, K. Ding, H. X. Han, G. H. Li, I. K. Sou, and W. K. Ge, Appl. Phys. Lett. **81**, 3170 (2002).

[29] H. M. Cheong, Y. Zhang, A. Mascarenhas, and J. F. Geisz, Phys. Rev. B **61**, 13 687 (2000).