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Ordering induced direct and indirect transitions in semiconductor alloys

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Atomic ordering from random alloys results in a peculiar evolution of electronic structures. Utilizing this property, we show theoretically that the directness of a band gap can be manipulated by forming ordered alloys in specific atomic configurations. For example, we show that Ga_4NAs_3 can have an indirect band gap if it forms the luzonite structure, despite that the constituents GaN and GaAs in the zinc-blende (ZB) structure, and their random alloys, all have direct band gaps. On the other hand, Al_2NP can have a direct band gap if it forms the CuPt structure, although the ZB constituents AlN and AlP, and their random alloys, all have indirect band gaps. These direct and indirect transitions are explained in terms of the ordering-induced evolution of the electronic states at high symmetry k points, namely, the emergence of the symmetry-enforced segregating states that are preferentially localized on one of the two sublattices in the ternary alloy, and the level repulsion between different ZB states that are folded into the same symmetry states in the ordered ternary alloy.

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I. INTRODUCTION

Band structure engineering is continually gaining more importance in semiconductor physics, because recent advances in semiconductor devices have increased the demands for new functional materials with unique physical properties.[1,2] Currently, the available natural semiconductors are very limited. To optimize for a specific device application, it is often desirable to design a semiconductor with a particular band structure. For example, many optical and electronic devices depend on the size and type of the band gap of the semiconductors, that is, whether the band gap is direct or indirect. Achieving high quantum efficiency usually requires that the semiconductors used for optoelectronic device applications have a direct band gap. On the other hand, to improve carrier lifetime for a transport device, an indirect band gap semiconductor may be more desirable.[3] Therefore, it is interesting to know if we can change the type of the band gap by converting an indirect semiconductor to a direct one, or vice versa. In the past, such a change of band gap and type (i.e., direct or indirect) can be realized by applying pressure. For example, for GaAs, its band gap can change from direct to indirect if its lattice constant is reduced by 1.7% from equilibrium value. The change can also be realized by forming alloys $A_xB_{1-x}C$ of semiconductors AC (which has an indirect band gap), with BC (which has a direct band gap).[4,5] One example is mixing the direct band gap semiconductor GaAs ($E_g = 1.5$ eV) with the indirect band gap semiconductor AlAs ($E_g = 2.2$ eV) to form a random alloy. The band gap of $Al_xGa_{1-x}As$ increases as the Al concentration x increases. When $x > 0.42$, the alloy converts from a direct gap to an indirect gap semiconductor.[6] However, despite many theoretical and experimental studies, it has never been shown until recently[7] that it is possible to convert alloys (e.g., GaN_xAs_{1-x}) from direct to indirect, when the constituents AC and BC are both direct, or vice versa.

In this paper, using first-principles band structure calculations, we show that through the control of atomic ordering in the alloys, it is possible to convert a direct band gap random alloy, e.g., $GaN_{0.25}As_{0.75}$, into an indirect band gap semiconductor compound Ga_4NAs_3, even though both GaN and GaAs are direct gap semiconductors. This can be done by arranging the atoms to form the luzonite structure [Fig. 1(a)], so that the segregating state[8] at $\bar{R}(L)$ (we use an overbar to indicate the k point of the superstructure; the k point in the parenthesis is the folded-in ZB k points)[5] is localized only on one constituent sublattice, whereas the complementary segregating states are localized only on the other sublattice. If one of the segregating conduction band states has lower energy than the averaged energy of the states at Γ, then the system could change from a direct gap semiconductor to an indirect gap semiconductor. As a counter example, we show that it is also possible to convert the indirect band gap semiconductor alloy $AlN_{0.5}P_{0.5}$ into a direct band gap semiconductor Al_2NP compound, even though AlN and AlP in the ZB structure are both indirect gap semiconductors.[6] This can be done by arranging atoms to form the CuPt structure [Fig. 1(b)], so that the ordering-induced band folding and resulting level repulsion[9] at Γ can push down the conduction energy level at Γ, making it the conduction band minimum (CBM) and the material direct.

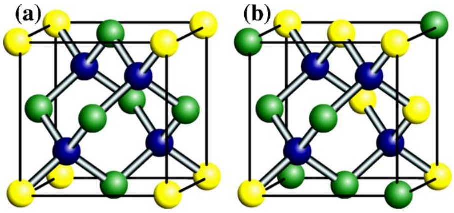

FIG. 1. (Color online) The atomic arrangement of (a) AB_3C_4 compound in the luzonite structure and (b) ABC_2 compound in the CuPt structure. Among ternary constituents atoms, type A atoms are represented with yellow, type B atoms with green, and type C atoms with blue balls.

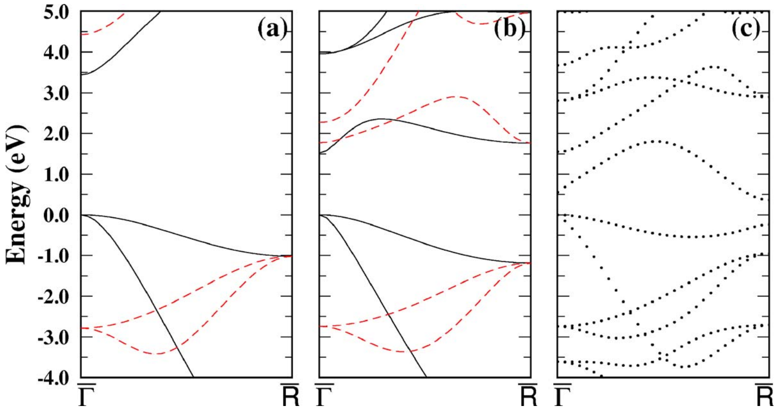

FIG. 2. (Color online) The band structure of (a) GaN, (b) GaAs in ZB structure, and (c) Ga_4NAs_3 in luzonite structure. For (a) and (b), bands along the Γ-L line are solid, and bands along the folded X-L lines are dashed. Note that (a) and (b) have direct band gaps at Γ, whereas in (c) the band gap is indirect with CBM at the $\bar{R}$ point.

II. METHOD OF CALCULATIONS

In this work, the band structure calculations were performed using the density functional formalism as implemented by the general potential, all electron, linearized augmented plane wave (LAPW) method.[10] We used the Ceperley-Alder exchange correlation potential[11] as parametrized by Perdew and Zunger.[12] The Brillouin zone integration of the superstructures is performed using special **k** points which are equivalent[13] to the ten special **k** points in the zinc-blende Brillouin zone. For the binary compounds, the band structures are calculated at the experimental lattice constants (4.50, 5.65, 4.36, and 5.47 Å for GaN, GaAs, AlN, and AlP, respectively).[6] For the alloys, we assumed the alloy lattice constants follow Vegard's rule[14]

$$a(x) = xa_{AC} + (1-x)a_{BC}. \qquad (1)$$

The random alloy is represented by the 32-atom special quasirandom structure (SQS16), which has atomic correlation functions similar to those of the random alloy.[15] The cell-internal structural parameters of the alloy is fully relaxed by minimizing the total energy and quantum mechanical forces at the atomic site.

It is well known that the first-principles LDA calculation severely underestimates the semiconductor band gap.[16] It also gives an incorrect energy separation among the L_{1c}, X_{1c}, and Γ_{1c} conduction band states, although the calculated order is usually correct. That is, AlN and AlP are indirect band gap materials with CBM states at X, whereas GaAs and GaN are direct band gap semiconductors with CBM at Γ.[16] The VBM always occurs at the Γ point. To overcome these problems, we used a well-established semiempirical approach to correct the LDA band gap error by adding to the LDA potential a δ-function-like external potential[17,16] inside the muffin-tin (MT) spheres centered at each atomic site α,

$$V^{\alpha}_{\text{ext}}(r) = \bar{V}^{\alpha} + V^{\alpha}_{0}\left(\frac{r^{\alpha}_{0}}{r}\right)e^{-(r/r^{\alpha}_{0})^2}, \qquad (2)$$

and performed the calculations self-consistently. To improve the transferability, no potential is added at the interstitial sites.[16] This potential pushes the s orbital energy upward, and thus increases the band gap. Because we are focused on the relative position of the L_{1c}, X_{1c}, and Γ_{1c} derived states in the alloy, in the fitting process, we tried to fit the energy separations among L_{1c}, X_{1c}, and Γ_{1c} as closely as possible to the available experimental data. A final scissor operator (a constant shift of the conduction band energy) is also used to get the correct band gap at Γ for the binary compounds. After the fitting, the calculated volume deformation potentials of the band gaps are in good agreement with the experimental data.[18] We want to emphasize that the final results for the directness of the band gap is not sensitive to the fitting process.

III. RESULTS AND DISCUSSIONS

A. Direct to indirect transition for $GaN_{0.25}As_{0.75}$

In the first example, we show how we can convert a direct gap random alloy into an indirect gap compound, even though both end-point constituents are direct gap semiconductors. In this case, we choose ZB GaN and GaAs, which are both direct gap semiconductors at their respective equilibrium lattice constants. Figures 2(a) and 2(b) plots the band structure of GaN and GaAs. For GaN, the fitted (experimental[18]) L_{1c} level is 2.78 (3.04) eV higher than the Γ_{1c} state, whereas the X_{1c} state is 0.99 (1.10) eV higher in energy. For GaAs, the fitted (experimental[18]) L_{1c} level is 0.24 (0.29) eV higher than the Γ_{1c} state, whereas the X_{1c} state is 0.25 (0.46) eV higher in energy. For the random alloy, the L_{1c}, X_{1c}, and the Γ_{1c} states each can be described as[4]

$$E^{i}_{g}(x) = (1-x)E^{i}_{g}(AC) + xE^{i}_{g}(BC) - b_{i}x(1-x), \qquad (3)$$

where b_i is the so called bowing parameter with $i{=}L$, X, and Γ. Because the bowing parameter b_{Γ} is similar or larger than b_L and b_X, the band gap of random GaN_xAs_{1-x} is also direct. For example, the calculated Γ_{1c} derived state of the $GaN_{0.25}As_{0.75}$ random alloy is about 0.6 eV lower in energy than the L_{1c}. This is quite general, i.e., when the constituents of AC and BC have direct band gaps, their alloy in the random configuration also has a direct band gap.

To covert this direct band gap alloy into an indirect band gap material, we rearranged the anions of $GaN_{0.25}As_{0.75}$ to form the Ga_4NAs_3 ordered compound in luzonite structure with eight atoms per unit cell [Fig. 1(a)]. In this ZB superstructure, each superlattice k point (labeled with an overbar) corresponds to four ZB k points. For example, the luzonite $\bar{\Gamma}$ point corresponds to the ZB Γ and three folded-in X points, whereas the luzonite $\bar{R}$ point corresponds to the four ZB L points. Therefore, the $\bar{\Gamma}$-$\bar{R}$ line in the luzonite structure corresponds to one ZB Γ-L line and three X-L lines. Figure 2(c) plots the calculated band structure of Ga_4NAs_3 in the luzonite structure along the $\bar{\Gamma}$-$\bar{R}$ line. We find that in this case, the conduction band edge state at $\bar{R}$, $\bar{R}_{1c}$, has a lower energy than the $\bar{\Gamma}_{1c}$ state at the zone center. That is, when the alloy forms the ordered luzonite structure from the random structure, its band gap changes from direct to indirect.

To understand this change, we notice that in the luzonite structure, the conduction band states at $\bar{R}$ are folded from the four zinc-blende L_{1c} states with mostly anion s and cation s characters. That is, the four L_{1c} ZB states become $\bar{R}_1$ (singly degenerate) and $\bar{R}_{15}$ (triply degenerate) states. By symmetry, the $\bar{R}_1$ state is almost completely localized on GaN (with no As s character), whereas the $\bar{R}_{15}$ state is almost completely localized on GaAs (with no N s character). In other words, the $\bar{R}_1$ and $\bar{R}_{15}$ are two segregating states.[8,5] This can be seen clearly by plotting the charge density of these two states (see Fig. 3). Because of this symmetry-imposed state segregation and because GaN has a very low L_{1c} energy at the alloy volume (see below), the GaN L_{1c} derived $\bar{R}_{1c}$ state energy is lower than the $\bar{\Gamma}_{1c}$ state energy, so the system becomes indirect.

The reason that the $\bar{R}_{1c}[L_{1c}(\mathrm{GaN})]$ state is very low in energy is due to the large volume deformation potential of GaN.[19] The volume deformation potential for the Γ_{1c} gap and the L_{1c} gap are both negative, i.e., when volume increases, the Γ_{1c} and L_{1c} energy decreases. For GaN, our calculations show that when its volume is deformed to the much larger alloy volume at $x=0.25$, the energy of its Γ_{1c} gap is reduced by 3.01 eV, whereas the L_{1c} gap is reduced by 2.96 eV. For GaAs, the band gap is increased by 1.21 and 0.45 eV, respectively. Because the state at Γ is not a segregating state, i.e., its energy level is close to the weight averaged value of the binary compounds, so it is higher in energy than the GaN L_{1c} derived $\bar{R}_{1c}$ state. The analysis above thus indicates that in order to reverse the order of $\bar{\Gamma}$ and $\bar{R}(L)$, the smaller constituents must have a large magnitude of volume deformation potential at L and a large lattice mismatch between the two constituents.

B. Indirect to direct transition for $AlN_{0.5}P_{0.5}$

In the following, we will show a counter example, i.e., converting an indirect gap random alloy into an direct gap material, even though both the end-point constituents of the alloy are indirect gap semiconductors. In this case, we choose ZB AlN and AlP as the end-point compounds, which have their VBM at Γ and CBM at X points at their respective equilibrium lattice constants. Figures 4(a) and 4(b) give the calculated band structure of AlN and AlP. For AlN, our fitted (experimental[18]) X_{1c} and L_{1c} levels are -1.62 (-1.09) and 2.96 (3.25) eV with respect to the Γ_{1c} level, respectively. For AlP, the fitted (experimental[18]) positions of the X_{1c} and L_{1c} levels are -2.15 (-1.91) and -0.56 (-0.85) eV with respect to the Γ_{1c} level, respectively. We find that random $AlN_{0.5}P_{0.5}$ indeed has the indirect band gap character. The Γ_{1c} derived state of the $AlN_{0.5}P_{0.5}$ random alloy is about 0.5 eV higher than the X_{1c} derived states.

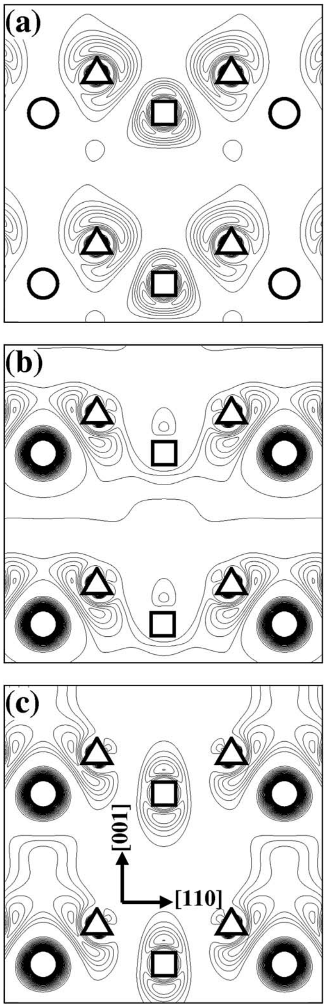

FIG. 3. Electronic charge density of (a) $\bar{R}_{15c}$ (second lowest conduction band state at $\bar{R}$), (b) $\bar{R}_{1c}$ (CBM at $\bar{R}$), and (c) $\bar{\Gamma}_{1c}$ (CBM at $\bar{\Gamma}$) for Ga_4NAs_3 in luzonite structure. The empty circle, square, and triangle corresponds to N, As, and Ga sites, respectively. Notice that the charge density localizes on the GaN sublattice for $\bar{R}_{1c}$ state, whereas it localizes on the GaAs sublattice for $\bar{R}_{15c}$ states. It is delocalized for the $\bar{\Gamma}_{1c}$ state.

To convert this indirect gap random alloy into a direct gap material, we rearrange the anions to form the CuPt structure, which corresponds to the ZB $(AlN)_1$ $(AlP)_1$ superlattice along the $[111]$ direction as shown in Fig. 1(b).[20] Because the unit cell volume for the superlattice is two times larger than that of the ZB constituent, two k points in the ZB Brillouin zone fold into one k point in the superlattice BZ. The periodicity along the $[111]$ superlattice direction is two times larger than in the ZB structure, so the $\bar{\Gamma}$ point of the CuPt structure contains ZB Γ and L_{111} points. On the other hand, the $\bar{D}$ point, another symmetry point in the CuPt structure, contains one of the other three ZB L points and one of the three ZB X points. The band structure for the CuPt structure is shown in Fig. 4(c) along the $\bar{\Gamma}$-$\bar{D}$ line and compared

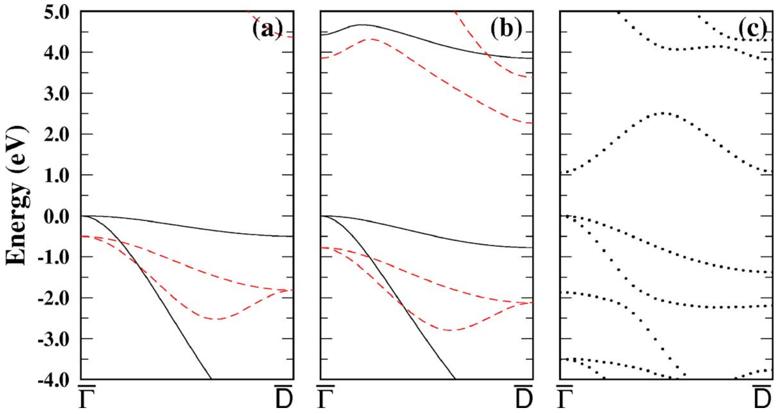

FIG. 4. (Color online) The band structure of (a) AlN, (b) AlP in ZB structure, and (c) Al_2NP in the CuPt structure. For (a) and (b), bands along the Γ-D line are solid, and the folded bands are dashed. Note that in (a) and (b), the CBM is at $\bar{D}$ point, whereas in (c) the band gap is direct with CBM at $\bar{\Gamma}$.

with the band structure of AlN [Fig. 4(a)] and AlP [Fig. 4(b)]along the same lines. One can see that after forming the ordered CuPt structure, the band gap is now direct with both VBM and CBM at the $\bar{\Gamma}$ point.

This change of directness originates from the repulsion between the $\bar{\Gamma}_{1c}(\Gamma_{1c})$ and the folded $\bar{\Gamma}(L_{111})$ states in the ordered CuPt structure. The repulsion is large at the $\bar{\Gamma}$ point because the coupling potential is commensurate with the superlattice period, and the wave function overlap of the Γ_{1c} and L_{1c} states are large (see Fig. 6). This large level repulsion leads to a large separation between the CBM and the L_{1c}-derived conduction band state at $\bar{\Gamma}$ (about 6.7 eV), and a strong wave function localization of these two states, as shown in Figs. 5(a) and 5(b). The CBM is now localized on the AlN sublattice because N is more electron negative than P, and AlN is expanded significantly when it forms the superlattice. On the other hand, the level repulsion between the states at $\bar{D}$ is much weaker, because the ZB X_{1c} state and the ZB L_{1c} state that fold into $\bar{D}$ have different atomic charge characters (the X_{1c} state has anion *s* and cation *p* characters, whereas the L_{1c} state has mostly anion *s* and cation *s* character, similar to that of Γ_{1c}, see Fig. 6). The charge density plot of the CBM state at $\bar{D}$ [Fig. 5(c)] confirms that it is not as localized as the CBM state at $\bar{\Gamma}$ and has mostly X_{1c} character. It is because of the strong level repulsion at the $\bar{\Gamma}$ point, that the CBM at Γ is pushed down below the lowest conduction band state at the $\bar{D}$ point, so the band structure becomes direct.

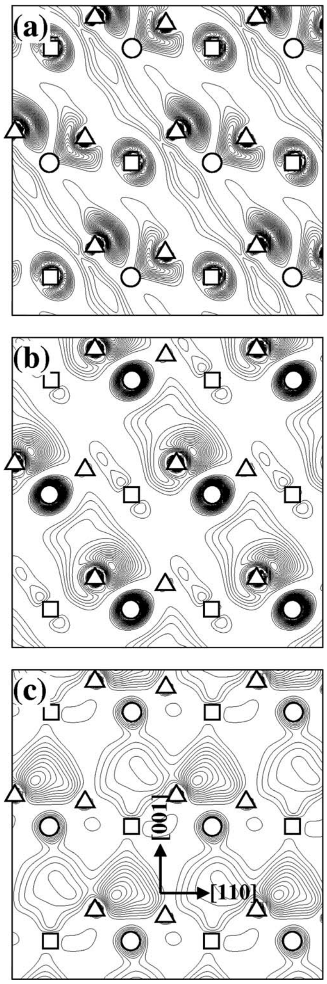

FIG. 5. Electronic charge density of conduction band states at $\bar{\Gamma}$ and $\bar{D}$ in superlattice BZ for Al_2NP. (a) is the L_{1c}-derived conduction band state at $\bar{\Gamma}$, (b) is the CBM at $\bar{\Gamma}$, and (c) is the lowest conduction band state at $\bar{D}$. The empty circle, square, and triangle corresponds to N, P, and Al sites, respectively. For (a), the charge density localizes preferentially on AlP sublattice, whereas for (b), it is localized on the complementary AlN sublattice. The charge density in (c) is less localized and has mostly X_{1c} character with charge in the interstitial region.

C. SUMMARY

In conclusion, we demonstrate the possibility of changing the directness of a semiconductor alloy by forming a specific ordered superstructure. For $GaN_{0.25}As_{0.75}$, the alloy can have indirect band gap if it forms the luzonite structure, although both ZB GaN and GaAs have direct band gaps. This results from the fact that the segregating $\bar{R}_{1c}$ state localizes on GaN sublattice feeling the GaN potential only, hence it becomes the CBM as the alloy lattice constant is larger than that of pure GaN, whereas the lowest conduction band level at the $\bar{\Gamma}$

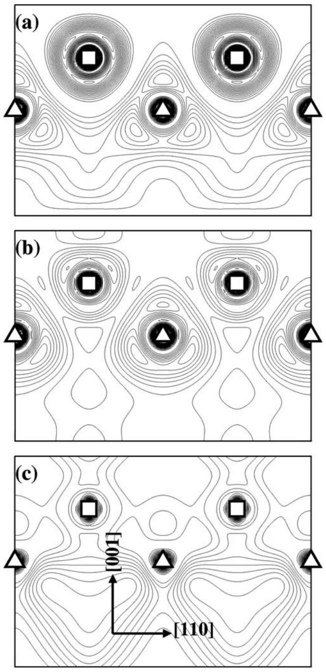

FIG. 6. Electronic charge density of (a) Γ_{1c}, (b) L_{1c}, and (c) X_{1c} states in ZB AlP. The empty square and triangle represent P and Al sites, respectively.

point is determined by averaging the two Γ_{1c} levels of ZB GaN and GaAs at the alloy lattice constant, and hence does not change much in energy. Our analysis suggest that this direct to indirect transition will most likely to occur in a system with (1) large lattice mismatch between the constituents and (2) the constituent with the smaller lattice constant having a large deformation potential for the L_{1c} state and possibly also low L point energy. For the $AlN_{0.5}P_{0.5}$ alloy, when it forms the CuPt structure, it becomes a direct band gap semiconductor although both the ZB AlN and AlP are indirect semiconductors. This is because there is a stronger level repulsion at the $\bar{\Gamma}$ point between the ZB Γ state and the folded ZB L state, whereas the repulsion at other symmetry points, such as $\bar{D}$, is relatively weak. Our analysis suggest that this indirect to direct transition will most likely to occur in a system with (1) small Γ-L separation in the conduction band and (2) large size and chemical mismatch between the constituents.

ACKNOWLEDGMENTS

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