Origination of the direct-indirect band gap transition in strained wurtzite and zinc-blende GaAs nanowires: A first principles study

Xihong Peng1,† and Andrew Copple2

1School of Letters and Sciences, Arizona State University at Polytechnic Campus, Mesa, Arizona 85212, USA
2Department of Physics, Arizona State University, Tempe, Arizona 85287, USA

(Received 8 January 2013; published 14 March 2013)

Recent work [Appl. Phys. Lett. 100, 193108 (2012)] has demonstrated that uniaxial strain applied to wurtzite (WZ) GaAs nanowires leads to an interesting direct-indirect band gap transition. Here, we explored the potential of strain engineering on electronic structures of one-dimensional WZ and zinc-blende (ZB) GaAs nanowires along the [0001] and [111] directions, respectively. The studied strain includes uniaxial strain, radial strain, and strain along zigzag and armchair directions in the cross section of the nanowires and shear strains. It was found that the WZ and ZB GaAs nanowires with a diameter of ~2 nm have an indirect band gap, whereas, bulk GaAs has a direct gap. The near-gap states (valence-band maximum/conduction-band minimum) are dominated by $s$ or $p$ orbitals of Ga or As atoms. The energies of these states respond very differently to the applied strains. For example, the energy increases with a positive uniaxial expansion while decreasing with a negative uniaxial compression. One of the most prominent examples is the greatly enhanced mobility in the strained Si nanochannel.

In Sec. II, the detailed calculation methods are introduced. The approach for band engineering to fit a particular application purpose.

I. INTRODUCTION

Tailoring electronic properties of semiconductor nanostructures has been critical for nanoscale applications. Among various tailoring methods, size and surface passivation/functionnalization are most commonly adopted. Collectively, mechanical strain was also found to have a great potential to tune electronic properties of nanoscale semiconductors and is receiving an increased amount of attention. Adventitious strain is almost unavoidable experimentally, but a more interesting case comes from intentionally introduced and controlled strains. One of the most prominent examples is the greatly enhanced mobility in the strained Si nanochannel.

Recently, it was demonstrated that band gaps of semiconductor nanostructures can be modulated effectively under moderate strain. The approaches introducing strain include lattice mismatch, functional wrapping, material doping, and direct mechanical application. It was also found that nanostructures maintain integrity under a much higher strain than their bulk counterpart, which dramatically expands the strength of applicable strain to nanostructures.

One-dimensional (1D) nanostructures, such as nanowires, of group III-V semiconductors have drawn extensive research interest in recent years. They are expected to play important roles as functional components in future nanoscale transistors, optical devices, photovoltaic cells, biosensors, etc. In particular, GaAs has been considered as a promising channel material for high-speed $n$-type metal-oxide semiconductors beyond Si-based technology.

GaAs has two different crystal structures—zinc blende (ZB) and wurtzite (WZ). In bulk, the ZB phase is energetically more favorable than the WZ phase. In nanoscale, however, the WZ phase, experimentially, was observed more often. Theoretical and experimental work has shown that, at small sizes, both WZ and ZB structures can be formed.

Although bulk GaAs (both ZB and WZ) has a direct band gap, a GaAs nanowire may demonstrate an indirect gap if its diameter is sufficiently small. This band gap transition could fundamentally alter the electronic properties of GaAs nanowires and, thereby, affects the function of the material. Recently, Copple et al. found that, by applying uniaxial strain, WZ GaAs nanowires experience an interesting direct-indirect band gap transition. Strain is demonstrated as an alternative approach for band engineering to fit a particular application purpose.
section of the nanowires, and lastly, shear strains. Conclusions are summarized in Sec. IV.

II. METHODOLOGY

The first principles density functional theory (DFT) calculations were carried out using the Vienna ab initio simulation package. The DFT local density approximation and the projector-augmented wave potentials were used along with plane-wave basis sets. The kinetic-energy cutoff for the plane-wave basis sets was chosen to be 300.0 eV. The energy convergence criteria for electronic and ionic iterations were set to be $10^{-4}$ eV and 0.03 eV/Å, respectively. The Ga 3d, 4s, and 4p, As 4s and 4p, and H 1s electrons were treated as valence electrons. The reciprocal space of a nanowire was sampled at $1 \times 1 \times 6$ using Monkhorst-Pack meshes. In band-structure calculations, a total of 21 $K$ points were included along the $K$ vector path from $\Gamma(0,0,0)$ to $X(0,0,0.5)$.

The 1D WZ GaAs nanowire was generated along the [0001] direction (i.e., the z axis) from the bulk WZ GaAs. The diameter of the WZ nanowire is 22.2 Å, constituted by 54 Ga and 54 As atoms (see Fig. 1) in the unit cell. The ZB GaAs nanowires were obtained along the [111] direction from the bulk ZB phase GaAs. The diameter of the ZB nanowire is 17.0 Å, formed by 37 Ga and 37 As atoms in the unit cell. The dangling bonds on the surface of the nanowires were saturated by hydrogen atoms to maintain the tetrahedral network of Ga/As atoms.

The initial axial lattice constants in the WZ and ZB nanowires were set to be 6.51 and 9.72 Å, respectively, which were taken from the relaxed lattice constant of the bulk WZ and ZB GaAs, respectively. In addition to the axial lattice constant, the lateral length of the simulation cell was chosen so that the distance between the wire and its replica (due to the periodic boundary condition) is more than $14 \, \text{Å}$ to minimize the interactions between the nanowire and its replica. The axial lattice constant in the GaAs wires was optimized through the technique of total-energy minimization. The optimized lattice constants in the WZ and ZB nanowires are 6.51 and 9.67 Å, respectively.

Once the optimized geometry of a nanowire was obtained, a series of different types of strain were applied to the nanowire. The studied strain includes uniaxial strain, radial strain, strain along a specific crystalline direction, and shear strain as shown in Fig. 2.

The uniaxial strain was applied by rescaling the axial lattice constant of the wire in the $z$ direction. For example, a +2% tensile strain was applied by rescaling the axial lattice constant to 102% of its optimized value; whereas, a −2% compressive strain was applied to scale the lattice constant to 98% of its optimized value. Under each given uniaxial strain, the coordinates of the atoms in the nanowires were fully relaxed via the technique of total-energy minimization.

In the case of radial strain, strain was isotropically applied to the cross section (i.e., the $x\, y$ plane) of the wires. For each applied radial strain, the axial lattice constant and $z$ coordinates of the wire were fully relaxed to reach the total-energy minimum.

We also applied strain along a particular crystalline direction in the cross section of the nanowires. Two particular directions were chosen, namely, the zigzag (i.e., the $x$ axis) and the armchair (i.e., the $y$ axis), shown in Fig. 2. In these two cases, strain was only applied to the $x$ (or $y$) coordinates of the atoms, whereas, all other coordinates including the axial lattice constant were fully relaxed.

The definition of shear strain at nanoscale is not unique. In this paper, simple shear strain is mathematically defined as

$$\tan \theta = \frac{d}{l},$$

where $l$ is the original length of a given line, $d$ is the amount of deformation perpendicular to that given line, and $\theta$ is the angle the sheared line makes with its original orientation. For example, in our study of shear strain in the zigzag direction [see Fig. 2(e)], $l$ is taken as the $y$ coordinate of the atoms, and $d$ is the displacement of the atoms along the $x$ direction. Similarly, we also applied shear strain to the $y$ direction. For each strain, the coordinates which held the strain were kept fixed while all other coordinates including the axial lattice constant were optimized through total-energy minimization.

Note that the strain extremes considered in this paper are beyond the elastic limit in bulk GaAs. However, the nucleation of defects, such as dislocations may become energetically unfavorable, especially in the small-size nanowires. As shown in recent experimental work performed by Wang et al., the GaAs nanowires can hold a significantly higher strain than 1%.

![FIG. 1. (Color online) Snapshots of the studied WZ and ZB GaAs nanowires. The diameter and composition of each wire in a unit cell are given on top. Dashed rectangles in the side views indicate the unit cell. The red, blue, and white dots represent Ga, As, and H atoms, respectively.](115308-2)
ORIGINATION OF THE DIRECT-INDIRECT BAND GAP

III. RESULTS AND DISCUSSION

The band gap of a semiconductor is defined as the energy difference between the conduction-band minimum (CBM) and the valence-band maximum (VBM). If CBM and VBM are vertically aligned at the same \( \Gamma \) point in its band structure, the band gap is direct; otherwise, it is called indirect. It is known that bulk WZ and ZB GaAs have a direct band gap with both VBM and CBM located at \( \Gamma \). However, our calculated band structures of the 1D WZ and ZB GaAs nanowires demonstrate an indirect band gap as shown in Fig. 3. VBM of both nanowires are located at \( \Gamma \), however, CBM is not at \( \Gamma \). For the WZ nanowire, the CBM is located at the conduction-band valley near \( X \), whereas, for the ZB nanowire, the CBM is located at \( X \). Previous work reported a similar indirect band gap for small-sized GaAs nanowires. Copple et al.\(^1\) reported that, for the WZ GaAs nanowires, the critical nanowire size for the direct-indirect band gap transition is \(~28 \text{ Å}\), estimated from DFT calculations. WZ nanowires with a diameter smaller than this critical size demonstrate an indirect band gap while wires larger than the critical size show a direct band gap.\(^1\) In the case of ZB GaAs nanowires, the critical size for the band gap transition was \(~40 \text{ Å}\), reported by Persson and Xu using tight-binding calculations.\(^3\) The diameters of our studied WZ and ZB GaAs nanowires in this paper are 22.2 and 17.0 Å, respectively, which are both smaller than their threshold sizes. The indirect band gap predicted in our paper is consistent with literature.

The calculated band gaps for the WZ and ZB GaAs nanowires are 1.603 and 2.008 eV, respectively. It is well known that DFT underestimates the band gap of semiconductors, and advanced GW methods can provide improved predictions in the band gap. However, for the size of the nanowires investigated in the present paper, GW is not applicable due to its extremely high demand on computing resources. The present paper is mainly focused on the variation in electronic properties, such as energy levels with strain.

Previous studies on Si nanoclusters showed that the energy

FIG. 2. (Color online) Schematics of the studied strains (a) uniaxial strain along the axial direction (i.e., the \( z \) axis), (b) radial strain in the cross section, (c) strain along the zigzag direction (i.e., the \( x \) axis), (d) strain along the armchair direction (i.e., the \( y \) axis), and shear strain in (e) the zigzag and (f) the armchair directions.

To obtain a practical feeling for applying strain, we estimated the stress which might be required. For example, to apply \(+2\%\) tensile uniaxial strain to the WZ GaAs nanowire, a calculated stress of 2.5 GPa may be required.

FIG. 3. (Color online) Band structures of the geometry-optimized WZ and ZB GaAs nanowires. Both demonstrate an indirect band gap. Energies are referenced at the vacuum level.
FIG. 4. (Color online) The effect of the uniaxial strain on the band structure of (a)–(e) the WZ GaAs nanowire and (f)–(j) the ZB nanowire. Positive and negative values of strain refer to the tensile and compressive uniaxial strains, respectively. Energies are referenced at the vacuum level. A direct band gap was found at $+4\%$, $-2\%$, and $-4\%$ in the WZ nanowire and at $+4.5\%$ for the ZB nanowire. For the relaxed WZ and ZB wires, labels $E_{\text{CB} - \Gamma}$, $E_{\text{CB} - v}$, and $E_{\text{CB} - X}$ represent the energies of the conduction bands at $\Gamma$, at the conduction band valley, and at $X$, respectively.

A. Uniaxial strain

The effect of the uniaxial strain on the band structure of the WZ and ZB GaAs nanowires is plotted in Fig. 4. As mentioned before, without strain, the WZ nanowire demonstrates an indirect band gap with the CBM located at the conduction-band valley near $X$ [labeled as $E_{\text{CB} - v}$ in Fig. 4(c)]. With uniaxial compression of $-2\%$ or $-4\%$, the CBM is shifted to $\Gamma$, demonstrating a direct band gap as shown in Figs. 4(a) and 4(b). When the nanowire is under $+4\%$ uniaxial tensile strain, it also shows a direct band gap at $\Gamma$. In the case of the ZB nanowire, the CBM is located at $X$ for the relaxed wire. Tensile uniaxial strain as large as $+4.5\%$ can convert the gap to be direct.

From Fig. 4, it was also observed that the value of the band gap can be tuned by the strain. For example, the gap shrinks under both positive and negative strains in the WZ nanowire. The DFT predicted gap for the relaxed WZ nanowire is 1.603 eV. And the gap shrinks to 1.133 and 1.308 eV for $-4\%$ and $+4\%$ strains, respectively.

As can be seen from Fig. 4, the direct/indirect band gap in the WZ nanowire is the result of the energy competition of the two CB states $E_{\text{CB} - \Gamma}$ and $E_{\text{CB} - v}$. The nanowire yields a direct band gap if $E_{\text{CB} - \Gamma}$ is lower than $E_{\text{CB} - v}$, otherwise, it has an indirect band gap. For the ZB nanowire, the direct/indirect band gap is determined by the energy competition of $E_{\text{CB} - \Gamma}$ and $E_{\text{CB} - X}$.

In order to determine the critical strain in which the direct-indirect band gap transition occurs, we plotted the...
The direct-indirect band gap transition occurs at about −0.8%, indicated by the dashed vertical lines. The VBM is the result of competition between states \(A\) and \(B\), and the band conductivity at \(\Gamma\) is the result of competition between states \(C\) and \(D\).

The energy variation with strain for states \(A - D\) is plotted. All energies are referenced at the vacuum level.

In order to understand the linear trends for states \(A - D\) and \(E_{CB - V}\) in Fig. 5, their electronic states, such as electron charge distribution and wave function, were examined. The wave-function character was examined by projecting the wave function onto \(s, p\), and \(d\) orbitals at each atomic site. It was found that state \(A\) is dominated by \(p_z\) orbitals at the sites of Ga and As, state \(B\) is dominated by partial \(p_x\) and partial \(p_y\) orbitals, and states \(C, D\), and \(E_{CB - V}\) are all dominated by \(s\) orbitals. Figure 6 presents their electron-density contour plots and schematics of the wave-function character.

Although states \(C\) and \(D\) are dominated by \(s\) orbitals, the phase factor of their wave functions shows a distinct difference. In state \(C\), the four atomic layers of atoms (As, Ga, As, and Ga), which are perpendicular to the \(z\) axis demonstrate a phase order of \(+, -, -\), and \(+\) as shown in Fig. 6(h). However, in state \(D\), that phase order is \(+, +, +\), and \(-\). Therefore, the Ga-As bonds along the \(z\) direction (formed by the middle two atomic layers) shows a bonding character in state \(C\) while displaying an antibonding character in state \(D\) (also see their electron-density contour plots).

As speculated in literature, such different energy trends with respect to strain may be due to the different strain responses from involved energy components. Here, through the exchange energy model (Heitler-London), we further demonstrated that this different energy response to strain can be originated from the bonding and antibonding natures of orbitals. Although this model is originally developed for the hydrogen molecule, it may still give us useful physical insight as long as the exchange integral is mainly considered from the nearest-neighbor atoms.

In this model of the hydrogen molecule, the energies of its bonding and antibonding states are given by the equations,

\[ E_{\text{bonding}} = 2E_0 + \frac{e^2}{R} + \frac{K + H}{1 + S^2}, \]
\[ E_{\text{antibonding}} = 2E_0 + \frac{e^2}{R} + \frac{K - H}{1 - S^2}, \]

where \(E_0\) is the energy for an isolated atom, \(K\) represents the classical Coulomb energy between the electron-electron and electron-ion interactions, and \(S\) is the overlap integral of the orbitals between different atomic sites, which is usually much smaller than 1. The square of \(S\) is even smaller. Therefore, the exchange integral term \(H\) may be playing a dominant role.
in determining the different energy variation behaviors with strain in the bonding and antibonding situations,

$$H = \int \int \psi_a^* (r_1) \psi_b^* (r_2) \left( \frac{1}{r_{12}^2} - \frac{1}{r_{2s}} - \frac{1}{r_{1b}} \right) \times \psi_b (r_1) \psi_b (r_2) dr_1 dr_2.$$  \hspace{1cm} (4)

From Eq. (4), the exchange term $H$ is contributed from either nonclassical electron-electron (i.e., $\frac{1}{r_{12}^2}$, positive) or electron-ion interaction (i.e., $-\frac{1}{r_{2s}} - \frac{1}{r_{1b}}$, negative). For $s$ orbitals, the contribution of the electron-ion interaction is dominated over the electron-electron interaction in the exchange term $H$. As the atomic distance increases (corresponds to a positive strain), the energy contributed from the electron-ion interaction is increased more rapidly compared to the energy reduction in the electron-electron contribution [see Eq. (4)], which results in an increased value for $H$. And an increased $H$ value causes the bonding energy $E_{\text{bonding}}$ to increase and the antibonding energy $E_{\text{antibonding}}$ to decrease based on Eqs. (2) and (3). This could be the reason for the different trends for states $C$ (bonding $s$ orbital) and $D$ (antibonding $s$ orbital) in Fig. 5(b).

However, the situation becomes different when the orbital is not an $s$ orbital. For example, bonding $p$ orbitals demonstrate a different energy trend with strain, compared to bonding $s$ orbitals. As mentioned before, state $A$ is dominated by $p_z$ orbitals. The phase order of the $p_z$ orbitals in the middle two atomic layers, which are perpendicular to the $z$ direction, are $+$ and $-$, respectively, as shown in Fig. 6(f). This phase order yields a strong bonding character of the $p_z$ orbitals in the $z$ direction (also see their electron-density contour plots). A positive tensile strain causes the energy of the bonding $p_z$ orbital of state $A$ to decrease, opposite to that of the bonding $s$ orbital of state $C$. This might be due to the spindle shape of the $p$ orbitals in which the electron density is quite high in the region between atoms. In this case, the contribution of the nonclassical electron-electron interaction in the exchange integral in Eq. (4) is dominating compared to the electron-ion interaction. As the atomic distance increases (corresponds to a positive strain), the energy contribution of the electron-electron interaction is decreased more significantly compared to the increase in the electron-ion contribution, which gives a reduced value for $H$. And the decreased $H$ value results in an energy reduction in the bonding state from Eq. (2). This explains the energy trends for state $A$ in Fig. 5(b).

In the case of state $B$, the wave function is dominated by partial $p_x$ and $p_y$ orbitals. The phase orders of the $p_x$ orbitals in the middle two atomic layers are $+$ and $-$, respectively, as shown in Fig. 6(g), which yields an antibonding character in the $z$ direction (also see the electron-density contour plots). However, the spindle shape of $p_x$ and $p_y$ orbitals causes the electrons actually concentrated in the $xy$ plane. The wave function overlapping in the $z$ direction is expected to be small and gives a nonbonding nature in the $z$ direction. Applying the uniaxial strain in the $z$ direction does not affect on the electronic orbital of state $B$ much, and its energy is insensitive to the uniaxial strain, which explains the flat curve of state $B$ in Fig. 5(b).

For the conduction band at the valley ($E_{\text{CB}, -v}$), it is clear that some Ga-As bonds along the $z$ direction show a bonding character while others display an antibonding character from its phase factor in Fig. 6(j). However, the electron contour plot in Fig. 6(e) reveals that the electron cloud is mostly concentrated on the center atoms. Therefore, its bonding/antibonding character should be determined by the center atoms. From the phase factor of the center atoms inside the dashed rectangle in Fig. 6(j), it shows an antibonding character. Thus, the energy variation trends with strain for this state should follow the same trends as state $D$, which is also dominated by antibonding $s$ orbitals. This conclusion is consistent with our data for $E_{\text{CB}, -v}$ in Fig. 5(a).

A similar analysis was also applied to the ZB nanowire, and the critical uniaxial strain of the band gap transition was found to be $+3\%$. The energy variation trends with strain for the near-gap states in the ZB nanowire follow the above general conclusions for the WZ nanowire.

**B. Radial strain**

Radial strain was applied to the cross section of the WZ and ZB GaAs nanowires. At each given radial strain, the $z$
coordinates of the atoms and the axial lattice constant of the nanowires are fully relaxed to reach the total-energy minimum. The effect of the radial strain on the band structure of the WZ and ZB GaAs nanowires is presented in Fig. 7. Take the example of the WZ nanowire, the direct band gap only occurs for the positive radial strain at $+2\%$ and $+4\%$. Within the strain range studied in this paper, no band gap transition occurs for the negative strain. In contrast, for the ZB wire, only a negative strain at $-4\%$ can have a direct band gap.

To estimate the critical radial strain needed to trigger the band gap transition, the energies of three near-gap states, $E_{C\text{B}-\Gamma}$, $E_{C\text{B}-\text{v}}$, and $E_{\text{VBM}}$, are plotted as a function of the radial strain. As an example, Fig. 8(a) shows the curves for the WZ GaAs nanowire. From the crossover of the two conduction bands, the critical strain for the direct-indirect gap transition was estimated to be $\sim +0.4\%$.

From further examination of three near-gap states at different values of radial strain, it was found that the VBM is the result of energy competition of two states $A$ and $B$, whereas, each conduction band ($E_{C\text{B}-\Gamma}$ or $E_{C\text{B}-\text{v}}$) corresponds to the same electronic state at different values of radial strain. State $A/B$ is the same state discussed in the previous section. And $E_{C\text{B}-\Gamma}$ is the previous state $C$. The energy variation in states $A$ and $B$ as a function of radial strain is presented in Fig. 8(b). The energy of state $A$ is more sensitive to the radial strain, compared to that of $B$. The energy shifts for states $A$ and $B$ as a function of radial strain are shown in Fig. 8(b).
and $B$ are 0.719 and 0.155 eV, respectively, in the range of ±4% radial strain.

Similar to the case of the uniaxial strain, the energy of state $B$ is insensitive to the radial strain due to its unique electronic structure, which is dominated by partial $p_x$ and $p_y$ orbitals. It is more interesting to note that the energy variation in state $A$ in Fig. 8(b) is opposite that of the uniaxial strain in Fig. 5(b). This could result from the Poisson effect. When a positive radial strain (i.e., expansion) is applied to the nanowire, the axial lattice constant of the nanowire shrinks, which is correlated to the case of a negative uniaxial compression. For example, when +2% (+4%) radial expansion is applied to the WZ nanowire, the resulting axial lattice constant shrinks to 99.1% (98.2%) of its original value. This corresponds to the case of −0.9% (−1.8%) uniaxial strain. When −2% (−4%) radial compression is applied, the resulting axial lattice constant expands to 101.2% (102.3%) of its original value, which is correlated to the situation of +1.2% (+2.3%) uniaxial strain. This fact yields the opposite energy trends for state $A$ with the radial and uniaxial strains. This situation was also applied to the two conduction bands ($E_{CB−Γ}$ or $E_{CB−Γ}$) in which their general energy variation trends in Fig. 8(a) are opposite to their counterparts in Fig. 5, respectively [note $E_{CB−Γ}$ in Fig. 8(a) corresponds to state $C$].

A similar analysis was applied to the ZB nanowires, and the critical radial strain for the direct-indirect band gap transition was found to be −1.4%.

C. Strain along a specific crystal direction in the cross section

We applied a strain along a particular crystal direction in the cross section of the GaAs nanowires. Two specific crystal directions are chosen in this paper, namely, the zigzag and armchair directions, which correspond to the $x$ and $y$ axes, respectively. It was found that applying strain in different directions results in different effects on the electronic band structure. For example, applying strain in the armchair direction is easier to trigger the direct-indirect band gap transition than that of the zigzag direction in terms of the strain energy.

The effect of the strain in the zigzag direction on the band structure of the WZ and ZB GaAs nanowires is plotted in Fig. 9. Similar to the radial strain, a compressive strain in the zigzag direction does not trigger the gap transition in the WZ wire. A sufficiently big expansion, such as +4%, can convert the indirect gap to direct. For the ZB wire, only a negative strain (−4%) can trigger the gap transition in the range of strain that we examined.
The critical strain in the zigzag direction needed to trigger the direct-indirect gap transition is estimated through the energy crossover of the two competing conduction bands. As an example, Fig. 10(a) displays their energy variations with strain for the WZ nanowire. The energy crossover of the two conduction bands occurs at +3%. Unlike the cases of the previous uniaxial and radial strains, the zigzag strain shows a less-profound effect on tuning the energies of conduction bands. For example, in the range of strain studied in this paper, the energy shifts for the conduction band at Γ are 0.412, 0.579, and 0.216 eV for the uniaxial, radial, and zigzag strains, respectively. And the energy shifts in the conduction band at the valley are 0.515, 0.368, and 0.224 eV, for the uniaxial, radial, and zigzag strains, respectively.

The VBM in Fig. 10(a) is the result of competition of two states A and E. State A is still the same state shown in Fig. 6. The strain effect on the energies of A and E is plotted in Fig. 10(b). It shows state E experiences an energy increase with a negative zigzag strain. The electron-density contour plot of state E is presented in Fig. 10(c). Examination of the wave function of state E reveals it is dominated by px orbitals. The sign of the wave-function phase factor shown in Fig. 10(d) suggests that state E has a bonding px character in the x direction. According to the above discussion on the bonding of px orbital of state A, a negative compressive strain in the z direction gives an increased energy for state A. Similarly here, a negative strain in the x direction results in an energy increase for state E, which is consistent with our data in Fig. 10(b).

The energy trend of state A with the zigzag strain is very similar to the case of the radial strain, which is not surprising because these two types of strains both are applied in the cross section of the nanowire. A positive strain applied radially or in the zigzag direction results in a shrink in the axial lattice constant of the nanowire due to the Poisson effect. For example, applying a −4%, −2%, +2%, or +4% strain in the zigzag direction yields the axial lattice constant of the WZ wire to be 100.72%, 100.42%, 99.89%, or 99.45% of its original value, respectively. In addition, the energy trends for the two conduction bands with the zigzag strain are also similar to their counterparts with the radial strain.

For the strain applied in the armchair direction, it was found that it requires a lower value of critical strain to trigger the direct-indirect band gap transition in these GaAs nanowires. From the energy crossover of the two competing conduction bands, the critical strain for the direct-indirect gap transition is estimated to be +1% and −2.2% for the WZ and ZB nanowires, respectively [see Fig. 11(a)]. Similar to the case of the zigzag strain, the energy shifts with strain for the three near-gap states in Fig. 11(a) are relatively small compared to the previous uniaxial and radial strains. For example, the energy shifts in the conduction band at the valley are 0.515, 0.368, and 0.180 eV for the uniaxial, radial, and armchair strains, respectively.

In Fig. 11(a), the VBM was found to be contributed by two competing states, namely, states A and F. Their energies as a function of the armchair strain are plotted in Fig. 11(b). The electron charge distribution and wave-function character of state F is presented in Figs. 11(c) and 11(d). The projection of the wave function reveals that state F is dominated by px orbitals. The sign of the phase factor suggests that state F shows strong bonding in the y direction. This unique wave-function character yields its energy trends with strain in Fig. 11(b) (see the above explanation for states E and A). State A is still the same state presented in Fig. 6, therefore, the energy variation trend of state A in Fig. 11(b) is similar to that of the zigzag strain in Fig. 10(b).

**D. Shear strain along the zigzag or armchair direction**

Shear strains along the zigzag and armchair directions were applied to the WZ GaAs nanowire. It was found that no direct-indirect band gap transition occurs with the strain range studied (up to +4%) in this paper. The effect of shear strain in the zigzag direction on the band structure of the WZ GaAs nanowire is presented in Figs. 12(a)–12(c). No negative shear strain is studied because a negative shear strain causes the same effect as the positive shear strain due to the symmetry of the nanowire and the definition of shear strain in Eq. (1).

It is clear that the shear strain plays a negligible effect on tuning the electronic band structure of the WZ GaAs nanowire.
This conclusion is further demonstrated in Fig. 12(d) in which the energies are plotted as a function of shear strain. Within the strain range, the energy shifts are 0.120, 0.123, and 0.112 eV for $E_{\text{VBM}}$, $E_{\text{CB} - \Gamma}$, and $E_{\text{CB} - \text{v}}$, respectively. These energy shifts are much smaller compared to those of all other strain types discussed above. There is no energy crossover for the two curves of $E_{\text{CB} - \Gamma}$ and $E_{\text{CB} - \text{v}}$ in Fig. 12(d), suggesting no direct-indirect band gap transition. Each state of $E_{\text{VBM}}$, $E_{\text{CB} - \Gamma}$, and $E_{\text{CB} - \text{v}}$ corresponds to the same electronic orbitals at different values of shear strain.

Similar behavior is also found in the case of the shear strain along the armchair direction. It was found that the shear strain in the armchair direction demonstrates an even smaller effect on turning the band structure. The energy shifts with strain for $E_{\text{VBM}}$, $E_{\text{CB} - \Gamma}$, and $E_{\text{CB} - \text{v}}$ are 0.110, 0.109, and 0.097 eV, respectively.

The negligible effect of the shear strains on the band structure might be resulting from the much smaller strain energy introduced by the shear strains to the GaAs nanowire. The strain energy is defined as the difference in the total energy between the strained and the relaxed nanowire. As an example, the strain energy as a function of the value of strain is presented in Fig. 12(e) for the WZ GaAs nanowire. Clearly, the shear strain energy is negligible compared to other strain types. The shear strain energy is less than 0.045 eV under $+4\%$ shear strain either along the zigzag or the armchair direction. The strain energy introduced by the radial strain is the largest given the same value of strains among all strain types studied in this paper. This is because, in the radial strain, two dimensions (both $x$ and $y$) are strained. The strain energies of the rest of the three strains, namely, the uniaxial strain and strain in the zigzag and armchair directions, are close given the same value of strains. This is due to the fact that, in these three types of strains, only one dimension is under strain.

In the previous sections, we reported the values of critical strains to trigger the direct-indirect band gap transition. Based on the information in Fig. 12(e), one can calculate the critical strain energies for the gap transition. The critical strain value and strain energy are listed in Table I. It requires the smallest strain energy as 0.05 eV through applying the radial strain to convert the indirect band gap of the WZ GaAs nanowire to a direct gap. Slightly higher strain energy is needed to realize the gap transition by applying either a uniaxial compression with 0.08-eV strain energy or an expansion along the armchair direction with 0.10-eV strain energy. It demands the highest strain energy as large as 0.64 eV to trigger the band gap transition through applying strain in the zigzag direction.
TABLE I. The critical strain value and strain energy to trigger the direct-indirect band gap transition in the WZ and ZB GaAs nanowires. No band gap transition was found for the shear strains (denoted as N/A, not available).

<table>
<thead>
<tr>
<th>GaAs phase</th>
<th>Strain type</th>
<th>Critical strain $\varepsilon$ (%)</th>
<th>Critical strain energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WZ</td>
<td>Uniaxial</td>
<td>$+2.8, -0.8$</td>
<td>$0.65, 0.08$</td>
</tr>
<tr>
<td></td>
<td>Radial</td>
<td>$+0.4$</td>
<td>$0.05$</td>
</tr>
<tr>
<td></td>
<td>In zigzag</td>
<td>$+3$</td>
<td>$0.64$</td>
</tr>
<tr>
<td></td>
<td>In armchair</td>
<td>$+1$</td>
<td>$0.10$</td>
</tr>
<tr>
<td></td>
<td>Shear in zigzag</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Shear in armchair</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>ZB</td>
<td>Uniaxial</td>
<td>$+3.0$</td>
<td>$0.41$</td>
</tr>
<tr>
<td></td>
<td>Radial</td>
<td>$-1.4$</td>
<td>$0.28$</td>
</tr>
<tr>
<td></td>
<td>In zigzag</td>
<td>$-3.2$</td>
<td>$0.42$</td>
</tr>
<tr>
<td></td>
<td>In armchair</td>
<td>$-2.2$</td>
<td>$0.23$</td>
</tr>
</tbody>
</table>

For the ZB nanowire, it was found that it requires less strain energy to convert the gap to a direct gap by applying radial strain or strain in the armchair direction with the strain energies of 0.28 and 0.23 eV, respectively, compared to that of the uniaxial and zigzag strains.

IV. CONCLUSION

To summarize, the origination of the direct-indirect band gap transition in the strained 1D WZ and ZB GaAs nanowires was explored using first principles DFT calculations. It was found that (1) the WZ and ZB GaAs nanowires with diameters

TABLE II. Wave-function character for the near-gap states and schematics representing their energy variation trends with various strains.

<table>
<thead>
<tr>
<th>State</th>
<th>Dominating orbital</th>
<th>Character</th>
<th>Schematic of energy trend with strain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Uniaxial</td>
</tr>
<tr>
<td>A</td>
<td>$p_z$</td>
<td>bonding in z-direction</td>
<td><img src="image1" alt="Diagram" /></td>
</tr>
<tr>
<td>B</td>
<td>$p_x/p_y$</td>
<td>nonbonding in z-direction</td>
<td><img src="image5" alt="Diagram" /></td>
</tr>
<tr>
<td>C</td>
<td>$s$</td>
<td>bonding in z-direction</td>
<td><img src="image9" alt="Diagram" /></td>
</tr>
<tr>
<td>D</td>
<td>$s$</td>
<td>antibonding in z-direction</td>
<td><img src="image13" alt="Diagram" /></td>
</tr>
<tr>
<td>CB at valley</td>
<td>$s$</td>
<td>antibonding in z-direction</td>
<td><img src="image17" alt="Diagram" /></td>
</tr>
<tr>
<td>E</td>
<td>$p_x$</td>
<td>bonding in x-direction</td>
<td><img src="image21" alt="Diagram" /></td>
</tr>
<tr>
<td>F</td>
<td>$p_y$</td>
<td>bonding in y-direction</td>
<td><img src="image25" alt="Diagram" /></td>
</tr>
</tbody>
</table>
of ~2 nm have an indirect gap, opposite that of their bulk counterparts; (2) the band structures of the nanowires can be significantly tuned by applying an external strain; (3) the indirect band gaps of the nanowires can be tuned into a direct gap by applying a radial strain, whereas, it needs the largest strain energy through applying strain in the nanowire to be a direct gap by applying a radial strain; (4) different types of strain show a different order to trigger the direct-indirect band gap transition in terms of the strain energy. It requires the smallest strain energy to convert the indirect band gap of the WZ nanowire to be a direct gap by applying a radial strain, whereas, it needs the largest strain energy through applying strain in the zigzag direction; (5) the origination of the band gap transition in each type of strain was detailed, discussed by examining the energy response of their near-gap band states with respect to strain. The wave-function character of the near-gap states and their energy response trends with various strains were summarized in Table II.

ACKNOWLEDGMENTS

The authors thank Arizona State University Advanced Computing Center for providing computing resources (Saguaro Cluster). F. Tang is acknowledged for the valuable discussions and a critical review of the paper. S. Caudle is also acknowledged for reviewing the paper.

To whom correspondence should be addressed: xihong.peng@asu.edu

41L. Hedin, Phys. Rev. 139, A796 (1965).