In this paper we present a systematic study of the atomic and electronic structure of GaAs nanowires using first-principles pseudopotential calculations. We consider six different types of nanowires with different diameters all grown along [111] direction and reveal interesting trends between cohesive energy and nanowire type with varying diameters. Generally, the average cohesive energy of nanowires with wurtzite stacking is higher than those with zinc blende stacking for small diameters. We found that most of the bare nanowires considered here are semiconducting and continue to be semiconducting upon the passivation of surface dangling bonds with hydrogen atom. However, the surface states associated with the surface atoms having two dangling bonds in zinc blende stacking occur in the band gap and can decrease the band gap to change the nanowire from semiconducting to metallic state. These nanowires become semiconducting upon hydrogen passivation. Even if the band gap of some nanowires decreases with increasing diameter and hence reveals the quantum confinement effect, generally the band gap variation is rather complex and depends on the type and geometry, diameter, type of relaxation and also whether the dangling bonds of surface atoms are saturated with hydrogen.

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I. INTRODUCTION

In a search to discover semiconductor materials and metallic interconnect for new generation miniaturized electronic devices, nanostructures have been a focus of attention. Electronic devices, such as transistors based on carbon nanotubes\(^1\), attracted interest in nanowires. Rod-like Si nanowires have been fabricated\(^2\) with a diameter 1.3-7 nm.\(^3\) It has been shown that such Si nanowires can display metallic, semiconducting and half-metallic properties depending on their functionalization.\(^4\) Being an alternative to silicon based microelectronics GaAs is one of the most important materials used in semiconductor physics. Due to the high electron mobility, GaAs always carried a potential of being used in high speed electronic devices. For example, GaAs/AlGaAs heterostructures\(^5\) have served as a media for the two dimensional electron gas studies.

Similar to bulk crystals researcher have envisioned GaAs nanowires to be a potential alternative for Si nanowires. Recent advances in fabrication technology made it possible to grow GaAs nanowires. They are grown by metal catalysts in vapor-liquid-solid (VLS) mechanism.\(^6\) Generally, GaAs nanowires are grown along [111] direction in zincblende (zb) structure, whereas nanowires with wurtzite (wz) structure with diameter as small as 10 nm are also observed.\(^7\) Several models were developed to predict the transition radius from wurtzite to zinc blende structure.\(^8,9\) Actually, there is no sharp transition but instead there are many different stacking configurations with very similar energies and more sophisticated models are needed to predict the ground state configuration. Together with the crystal structure, surface facet structure is also an important parameter affecting the structural and electronic properties. Nanowires reported so far are either grown in zb structure with [112] or [110] facet orientation or in wz structure with [1100] or [1120] facet orientation.\(^10,11,12\) One of the unusual structures is so called A-wire, which has been grown in defect free triangular shape on (111)A surface of GaAs.\(^13\) More complex structure of nanowires grown on GaAs(111)B surface have been also reported.\(^14\)

There are many experimental and theoretical works on growth and structure of GaAs nanowires, but not much work is done to predict the electronic properties of these wires. Theoretical studies so far have focused on the electronic properties of superlattices composed of GaAs nanowires. For example, the electronic structure of InAs/GaAs nanowire superlattices with radius R=10 nm was examined using a semiempirical \(sp^3d^5s^*\) tight-binding model.\(^15\) Another atomistic tight-binding calculation was carried out to reveal the electronic structure of freestanding GaAs/Al\(_{0.3}\)Ga\(_{0.7}\)As nanowire superlattices oriented along the [100] crystallographic direction.\(^16\) Also a first-principles investigation has been performed on the hexagon-shaped, [111]/[0001]-oriented III-V semiconductor nanowires, which was concentrated on the surface effects on the structure and stability of these nanowires.\(^17\)

The purpose of this paper is to provide a detailed analysis of GaAs nanowires, which is necessary for further experimental and theoretical studies. To this end we present a systematic, first-principles investigation on structural and electronic properties of GaAs nanowires grown along [111] direction. Six different types of GaAs nanowires are distinguished depending on the shape of their cross sections and the crystallographic orientation of their side surfaces. Their optimized atomic structure and cohesive energies are calculated revealing interesting trends between atomic structure and cohesive energy. Based on the calculations of electronic structure and iso-
surface charge density of specific states we analyzed the character of states at the band edges and variation of band gap with diameter. The effects of hydrogen saturation of dangling bonds of surface atoms on the atomic and electronic structure are examined. We found that most of bare GaAs nanowires are semiconducting and remain semiconducting even before the passivation of surface dangling bonds. Only one type is metallic due to the states localized at the surface.

II. METHODS

We have performed first-principles plane wave calculations within Density Functional Theory (DFT) using ultrasoft pseudopotentials. A plane-wave basis set with kinetic energy up to 250 eV is used. The exchange correlation potential is approximated by generalized gradient approximation (GGA) using PW91 functional. For partial occupancies we use the Methfessel-Paxton smearing method. The adopted smearing width is 0.1 eV for the atomic relaxation and 0.01 for the accurate band structure analysis and density of state calculations. All structures have been treated within a supercell geometry using the periodic boundary conditions. In the self-consistent potential and total energy calculations the Brillouin zone (BZ) is sampled in the k-space within Monkhorst-Pack scheme by (1x1x9) mesh points for wz and (1x1x7) mesh points zb nanowires. All atomic positions and lattice constant are optimized by using the conjugate gradient method where total energy and atomic forces are minimized. The criterion of convergence for energy is chosen as $10^{-5}$ eV between two ionic steps, and the maximum force allowed on each atom is 0.05 eV/Å.

III. STRUCTURES AND COHESIVE ENERGIES

GaAs nanowires studied here are cut from ideal bulk structure along [111] direction. Nanowires having wurtzite (wz) and zinc blende (zb) stacking have four and six atomic layers in the unit cell, respectively. Except A-wire, they have hexagonal cross section. A-wires, by themselves have zb stacking and display a triangular cross-section with three (112) planar side surfaces. Atomic structures of cross-section of all nanowires are shown before and after relaxation (structure optimization) in Fig. 1. Here we consider the largest members of all types of GaAs nanowires. Upon relaxation the surfaces of ideal wires undergo a reconstruction, while inner parts preserve the bulk configuration. In spite of the fact that the indices of their planar side surface are the same, wz1 and wz3 are still different. wz3 structure have six identical surfaces, whereas wz1 structure have three surfaces same as wz3 and three surfaces with hanging Ga-As atom pairs before relaxation.

At the surfaces of some ideal structures in Fig. 1 the
atoms can have the coordination number smaller than four. Upon relaxation the coordination numbers may undergo a change. Two adjacent surface atoms having low coordination number can form new bonds, whereby these atoms increase their coordination number and the nanowire, in turn, lowers its energy (i.e., it becomes more energetic). It turns out that, the coordination number of surface atoms is crucial for the value of the cohesive energy per atom pair. For example, wz1 nanowire with \( N = 109 \) has three surfaces each having an atom pair with coordination number two, while other three surfaces have surface atoms with coordination number three. wz2 nanowires having \( N = 25, 60 \) and 85 atom pairs in the unit cell have surface atoms with coordination number two only at the corners of the hexagonal cross-section. On the other hand, wz2 nanowires having \( N = 42 \) and 114 atom pairs in the unit cell and all members of wz3 nanowires have surface atoms with coordination number three. In light of these arguments one expects wz3 to have larger cohesive energy per atom pair than the rest of wz2 nanowires, which, in turn, should be larger than that of wz1 nanowires. These arguments are actually confirmed in Fig. 2, where we present the trends of cohesive energies per atom pair for all nanowires considered here.

Ideal A-wires have surface atoms with coordination number of two on each surface, but apart from that, it has a triangular cross-section, which makes the surface to volume ratio even higher compared to that of other types. Consequently, A-wires have the lowest cohesive energy per atom pair as seen in Fig. 2.

Interestingly, wz structures have relatively larger cohesive energies than zb structures, with wz3 structure being the largest. The bulk zb structure however, is energetically more favorable than that of wz structure by nearly 20 meV per Ga-As pair, also confirmed by our calculations. As radii increase, the cohesive energy per Ga-As atom pair values should converge to the bulk value. It is energetically easier to form a wz surface than to form a zb surface. In other words, surface energy of zb structure is larger. That is why, wz structures become energetically more favorable as the surface to volume ration increases, namely as the radius of the nanowire decreases. So there should be some point where cohesive energy of wz and zb structures cross each other. The radius at this point can be interpreted as the critical radius for transition from wz to zb structure or vice versa. Here it should be noted that, energetically favorable does not mean that these structures will start to grow in experiments. One should also include effects of formation path, like nucleation growth. Actually, when we are around the critical radius we can see some hybrid stacking patterns like ABAC, which is defined as 4H structure.

Table I gives the calculated values for the structure and cohesive energies of nanowires after the relaxation. Cohesive energies per Ga-As atom pair increase with increasing diameter, approaching the bulk values, but we don’t see the critical radius because it is expected to be an order of magnitude larger than that of our nanowires. Surprisingly, the lattice constant decrease as the diameter of nanowires in zb structure increase, while for wz structures the reverse situation occurs. The ratio of number of surface atoms to the total number of atom pairs give a measure of surface to volume ratio, which is decreasing with increasing diameter. Note that the number of surface atoms having coordination number of two is \((N_D - N_S)\).

### IV. ELECTRONIC STRUCTURE

Most of the relaxed GaAs nanowires presented in Fig. 1 are semiconducting even without hydrogen saturation. As we will see, in some cases these bare GaAs nanowires don’t even have the surface states at the band edges. This situation is in contrast with Si nanowires. Si nanowires as cut from the bulk crystal and subsequently relaxed are found to be metallic. Their metallicity occurs due to the partial filling of the dangling bonds surface states. Upon passivation of the dangling bonds with hydrogen atoms the surface states are discarded from the band gap and eventually Si nanowire becomes semiconductor. In what follows, we will examine the electronic structure of bare GaAs nanowires and reveal the effects
TABLE I: Calculated cohesive energy per Ga-As atom pair $E_c$, band gap $E_g$, lattice constant along the wire axis $c$ and diameter $D$ values of relaxed nanowires are given. $D$ is defined as the largest distance between two atoms in the same cross-sectional plane. Here $N$ stands for the number of Ga-As atom pairs in the unit cell. $N_s$ and $N_d$ stand for the number of surface atoms and the total number of dangling bonds, respectively. Surface atoms are defined as atoms making less than four bonds, while the protruding bonds are defined as dangling bonds.

| Type | $wz1$ | $wz2$ | $wz3$ | $A$ | $zh1$ | $zh2$ |
|------|-------|-------|-------|-----|------|------|
| $N$  | 31    | 64    | 109   | 24  | 54   | 96   |
| $E_c$(eV) | 7.71 | 7.89 | 8.01 | 7.94 | 8.05 | 8.11 |
| $E_g$(eV) | 1.06 | 1.02 | 0.92 | 0.81 | 0.77 | 0.85 |
| $c$(Å) | 6.64 | 6.63 | 6.63 | 6.66 | 6.61 | 6.63 |
| $D$(Å) | 15.9 | 23.6 | 31.6 | 14.5 | 18.1 | 23.1 |
| $N_s$ | 24   | 36   | 48   | 24  | 36   | 48   |
| $N_d$ | 30   | 36   | 54   | 27  | 36   | 48   |

Figure 3 presents results of the band structure and charge density analysis performed for $wz1$ structure. Ideal structure of these wires have Ga-As atom pairs hanging on three surfaces, while other three surfaces have the same profile as $wz3$ type. Upon relaxation these hanging pairs tend to bend towards each other and lower energy by making unusual Ga-Ga and As-As bonds. For example, $wz1$ structure having 64 atom pairs per unit cell ($wz1–64$) have four hanging pairs before relaxation. After relaxation first two and last two of them bend to each other and form a stable structure. $wz1–31$ and $wz1–109$ nanowires have one hanging pair after relaxation. As a result, all surface atoms of $wz1–64$ structure have coordination number of three, while $wz1–31$ and $wz1–109$ have six surface atoms with coordination number of two (See Table I). Isosurface charge densities show that three states at the top of the valence band edge of $wz1–64$ and $wz1–109$ structures have bulklike character, while conduction band edge states concentrate at the surface. It is hard to define the nature of states in $wz1–31$ structure because it has low diameter. To calculate the band structure of the relevant surface we cut a slab from the bulk wurtzite structure parallel to (01¯10) surfaces so that the resulting structure have 11 atomic layers. This slab has two dimensional periodicity in the surface and a vacuum region between adjacent surfaces, so that they don’t interact. The band structure of this slab plotted along $k$, parallel to [111]-direction, provide us with information about the band structure of nanowires if they were grown thick enough to have a reasonable bulk region in order to reduce the corner effects. One expects the band gap of the infinite slab structure to be lower than that of the nanowires. Comparison of the bands of $wz1–109$ with those of (0110) surface confirm their similarity and expected size effect.

Figure 4 shows the band structure and charge density analysis for $wz2$ structures. Here all surface atoms of $wz2–42$ and $wz2–114$ structures have coordination number of three, while the rest of considered $wz2$ structures have surface atoms with coordination number of two at the corners. Note that the valence band edge of $wz2–42$ and $wz2–114$ structures mimic that of infinite slab structure, while other structures fail to do that. We see that the band gap of $wz2–42$ is larger than that of $wz2–114$ structure in agreement with the quantum confinement effect. On the other hand, however, $wz2–25$ structure have the lowest band gap. This is caused by large surface to volume ratio, which make surface effects pronounced. Isosurface charge densities show that the valence band edge have bulklike character, while conduction band edge states concentrate on the surface.

Band structure and charge density analysis of $wz3$ structure is illustrated in Fig. 5. This structure has the largest cohesive energy per atom value compared to other types of nanowires in Fig. 1. In this nanowire all surface atoms make three bonds and surface states derived therefrom do not occur in the band gap. Consequently, the band structure of the related infinite slab is very similar to that of $wz3–96$ nanowire. Charge density of the states at both band edges are spread throughout the nanowire cross-section showing the bulk character. Since band gap is not diminished by surface states bands, one can clearly see the quantum confinement effect in these nanowires.

Figure 5 also includes information about the effect of hydrogen passivation of all surface dangling bonds on the band structure of $wz3$ nanowires. In contrast to Si nanowires (where surface states of bare structure were carried out from forbidden region to the band continuum upon passivation with hydrogen), the band edge states of $wz3$ GaAs nanowires remain in their place after the hydrogen saturation. This conclusion is corroborated by the analysis of isosurface charge density of states at the center of BZ located at both edges of band gap. We found that the character and charge distribution of these states do not undergo a change after passivation of surface dangling bonds with hydrogen atoms. Also the similarity in the profile of band edges before and after hydrogen saturation is found to be striking. Here the increase of the band gap occur not because the edge states are cleared out, but because the atomic structure of the nanowires...
become more bulklike. This effect is illustrated in Fig. 6 where we analyzed the interatomic distance distribution of \( \text{wz3-96} \) structure before and after the hydrogen saturation. Plots given here are done by making a histogram of interatomic distances and then smearing it out. The first plot indicates the interatomic distance distribution of the core region of bare nanowire. We get the same result also in the core region of hydrogen saturated structure and the peaks match the first, second, third and fourth nearest neighbor distances of bulk GaAs in \( \text{wz} \) structure. The crucial difference between bare and hydrogen saturated structures is reflected in the shell part of the nanowires. One can clearly see that hydrogen saturated structure have more bulklike character.

Furthermore we performed atom projected density of states analysis by calculating the localized density of states on the surface atoms, as well as on the core atoms before and after passivation with hydrogen atoms. As seen in Fig. 6(d) and (e), surface as well as core atoms have comparable contributions to the state distribution at both edges of band gap. These results further corroborate the fact that GaAs nanowires like \( \text{wz3-96} \) having surface atoms with coordination number of three do not have dangling bond surface states in the band gap. For nanowires with large \( D \) the passivation with hydrogen have negligible effects on the band gap. Note that the increase in the band gap with decreasing diameter holds also for hydrogen saturated structures.

In Fig. 7 we present the band structures and isosurface charge densities of selected states at \( \Gamma \)-point of A-wires. Note that, we cannot have an infinite slab corresponding to the large A-wires because these nanowires have triangular cross-section. All relaxed A-wires have surface atoms with coordination number of two. The band gap have no obvious trend with varying diameter and is determined by surface states especially falling in the conduction band edge. For small \( D \) the edges of band gap are determined by surface states with low dispersion. As the diameter increases the valence band edge starts to show bulk character, while states at the conduction band edge remain to display surface character.
FIG. 6: Interatomic distance distribution of the core and shell part of bare and hydrogen saturated \( \text{wz}-96 \) structures. The ball and stick model illustrates the structure of \( \text{wz}-96 \) nanowire, while the shaded regions defines the core and shell parts of the nanowires. (a) Interatomic distance distribution of interior atoms of bare nanowire. (b) Interatomic distance distribution of exterior atoms of bare nanowires. (c) Interatomic distance distribution of hydrogen passivated exterior atoms. (d) Local density of states (LDOS) on surface atoms (green/light) and on the remaining atoms (blue/dark) of bare nanowire. (e) Same as (d) after passivation of surface atoms with hydrogen.

FIG. 7: Band structure and charge density isosurface plots for A-wires.

FIG. 8: (Color online) Band structure and charge density isosurface plots of GaAs nanowires having zb1 structure. Energy band gap between the valence and conduction band of bare nanowire is (yellow) light-shaded. Numerals given on top of the bands stand for the number of GaAs atom pairs \( N \) in the unit cell. Charge density isosurfaces of specific states at \( \Gamma \)-point are shown on the right hand side of the bands they belong to. Isosurface charge densities correspond to three valence and three conduction band edge states, ordered in the same manner as bands themselves are. Here we also give the band structure of infinite slab of bulk wurtzite structure with the same planar \((11\overline{2})\) surfaces as zb1 nanowires does. Zero of energy is set at the Fermi level \( E_F \). The widening of the band gap upon the termination of dangling bonds by hydrogen is shown by (green) dark-shaded regions for \( N = 31, 73 \) and surface.

Even for \( A-82 \) nanowire the flat band states at the edge of the conduction band are located on one of the planar side surface.

The effect of surface states on the band gap is dramatic for the bare GaAs nanowires having zb stacking. The values of band gap as large as 1.5 eV occurring in \( \text{wz} \)-type nanowires reduce to the values as small as \( \sim 0.2 \) eV in zb1-type nanowires. The calculated band gap can even be closed in zb2-type nanowires. It appears that many of the dangling bond surface states, in particular those associated with the surface atoms having coordination number of two, are placed in the band gap. Therefore one expect dramatic changes in the electronic properties after the passivation of surface dangling bonds with hydrogen atoms. The electronic structures of bare zb1-type nanowires are illustrated in Fig. Here all surface atoms of zb1 – 31 and zb1 – 113 nanowires have coordination number of three after relaxation, but certain surface atoms of zb1 – 73 structure cannot find a pair to form a bond and stay with coordination number of two. As a result the band gap of zb1 – 73 does not have a value between that of zb1 – 31 and zb1 – 133, as one would expect. To get more information about the na-
FIG. 9: Same as in Fig. 8 but for zb2 structure. The shaded region in the band structure of zb2 – 37 corresponds to the band gap opened after the passivation of dangling bonds with hydrogen. zb2 – 19 and zb2 – 61 nanowires are not passivated with hydrogen.

V. CONCLUSIONS

We have performed first-principles DFT calculations to reveal the atomic and electronic structure of six different types of GaAs nanowires. Nanowires considered have a diameter less than 3 nm, and at this sizes wz3-type have the highest cohesive energy per atom pair, while A-wires have the lowest. In general, wz nanowires have higher cohesive energy than zb nanowires, but the difference in cohesive energies decrease with increasing diameter.

We found that all wz- and A-type bare GaAs nanowires are semiconducting, except zb2-type. In general, for bare GaAs nanowires with surface atoms all having coordination number of three, the dangling bond states associated with these surface atoms do not appear in the band gap, but rather in the band continua. Quantum (size) confinement effect occurs in the band gap variation of these nanowires. For these nanowires the band gap may increase upon the passivation of dangling bonds with hydrogen, since bonding of surface atoms become more bulklike. On the other hand, dangling bond states of atoms having coordination number of two fall in the band gap and break this trend. Hydrogen saturation dramatically increases the band gap of the latter structures by clearing the surface states from the forbidden region. Generally, increasing diameter results in more bulklike valence band edge, however conduction band edge behave more surface like.

The band gap variation of GaAs nanowires is rather complex and depends on their type and geometry, diameter, relaxation and also whether the dangling bonds of surface atoms are passivated with hydrogen. We believe that present results are valuable for further research on GaAs and other III-V compound nanowires dealing with their doping, forming heterostructure and multiple quantum well structure and their functionalization to get new electronic and magnetic properties.

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