Structures, stabilities, and electronic properties of GaAs tubelike clusters and single-walled GaAs nanotubes*

Liu Li-Ren(刘立仁)[a], Zhu Heng-Jiang(祝恒江)[a]†, Liu Zhi-Feng(刘志锋)[b], and Wu Peng(吴 鹏)[a]

[a] *School of Physics and Electronic Engineering, Xinjiang Normal University, Urumchi* 830054, *China*
[b] *College of Physics, Chongqing University, Chongqing* 401331, *China*

(Received 2 July 2012; revised manuscript received 26 August 2012)

The geometric structures, stabilities, and electronic properties of $(GaAs)_n$ tubelike clusters at up to $n = 120$ and single-walled GaAs nanotubes (GaAsNTs) were studied by density functional theory (DFT) calculations. A family of stable tubelike structures with a Ga–As alternating arrangement were observed when $n \geq 8$ and their structural units (four-membered rings and six-membered rings) obey the general developing formula. The average binding energies of the clusters show that the tubelike cluster with eight atoms in the cross section is the most stable cluster. The size-dependent properties of the frontier molecular orbital surfaces explain why the long and stable tubelike clusters can be obtained successfully. They also illustrate the reason why GaAsNTs can be synthesized experimentally. We also found that the single-walled GaAsNTs can be prepared by the proper assembly of tubelike clusters to form semiconductors with large band gaps.

Keywords: $(GaAs)_n$ tubelike clusters, GaAs nanotube, density functional theory, electronic property

PACS: 36.40.Qv, 36.20.Kd, 61.46.Fg, 71.15.Mb **DOI:** 10.1088/1674-1056/21/12/123601

1. Introduction

Recently, low-dimensional semiconductor materials have become of great interest to researchers in nanoscience.[1−4] Among these materials, III–V group semiconductor compounds have drawn much attention because of their paramount technological potential applications,[5−16] such as optoelectronic device, photonics integrations, ultrahigh frequency microwave, ultrahigh-speed microelectronic device, and photovoltaic solar cells.

Gallium arsenide (GaAs), as a substantial member of the III–V group semiconductor compounds, has many distinctive properties, such as low electronic effective mass, high-electron mobility, and high-saturation drift velocity, which makes it ideal for optoelectronic, low power, and ultrahigh-speed device application. Moreover, it is an advantageous material for making nanoscale devices because its surface Femi level pinning in the conduction band does not become an insulator due to depletion of carriers. Hence, for the past decades, there have been a great number of studies investigating the chemical and physical properties of its nanostructure. For instance, it was found that BN fullerene structures and structures containing pentagons are competitive for being the geometry of the lowest energy state of small neutral[17] and charged[18] $(GaAs)_n$ clusters. Beginning with $n = 14$, all the lowest energy states of $(GaAs)_n$ clusters possess BN-fullerene topologies until a state with the bulk-type geometrical configuration composed of the 12-atom bulk core and BN-fullerene surface becomes[18] the lowest total energy state at $n = 36$. Ghosh *et al.*[19] have studied zigzag and armchair single-walled GaAs tubes of different diameters using the density functional theory (DFT) with a tight-binding approximation. They found that the GaAs tubes are semiconducting and that the band gaps in the armchair tubes are more than twice as wide as those in zigzag tubes of similar diameters.

Although several theoretical and experimental studies have been carried out, few studies focus on the structures, stabilities, and electronic properties of $(GaAs)_n$ tubelike clusters and infinite single-walled GaAs nanotubes (GaAsNTs). To our knowledge, nanoclusters or nanotubes can be considered as the transi-

*Project supported by the Key Subject of Theoretical Physics of Xinjiang Uygur Autonomous Region (Young Teachers Scientific Research Fund), China, the Natural Science Foundation of Xinjiang Uygur Autonomous Region, China (Grant No. 2010211A21), and the Key Project of Higher Education of Xinjiang Uygur Autonomous Region, China (Grant No. xjedu2009i27).

†Corresponding author. E-mail: zhj@xjnu.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

tional forms between atoms and bulk, and their fundamental properties depend crucially on the size.[20−22] Therefore, it is possible to tune the physical and chemical properties of these nanostructures by changing their size, making them promising materials for numerous applications. Apparently, to understand the unique properties of tubular GaAs nanostructures on different nanometer scales, the structures and electronic properties of GaAs tubelike clusters and nanotubes should be clarified first. Therefore, this study intends to investigate stoichiometric $(GaAs)_n$ ($n \leq 120$) tubelike clusters and GaAsNTs by using the DFT method, and especially to seek the answer to the following questions: 1) are there any laws applicable to the structural growth of clusters and GaAsNTs? 2) How about their stabilities and electronic properties, such as binding energy, HOMO–LUMO energy gaps, and energy band structures? 3) Why can the stable one-dimensional tubular structures be obtained in the previous experimental study and our theoretical calculation? 4) Are the small-bore tubelike clusters and GaAsNTs still conductive or semiconductive with a narrow band gap?

2. Computational details

This research examines the structures and characteristics of tubelike $(GaAs)_n$ ($n \leq 120$) clusters by using the DFT with unrestricted B3LYP exchange-correlation potential.[23,24] To better describe the bonding and geometrical features of heavy atoms, the basis set, effective core potential LanL2DZ,[25] was adopted in this study for both arsenic (As) and gallium (Ga) atoms. Under this basis set, the outermost valence electrons $3s^23p^63d^{10}4s^24p^1$ for Ga, $3s^23p^63d^{10}4s^24p^3$ for As were described and their core electrons were not taken into account. The processes of optimization were based on energy system convergence, and the convergence of energy was better than 10^{-6} a.u. (a.u. is the atomic unit). In order to save time and improve efficiency, the processes were to optimize the structures with a prescribed bond length, bond angle, and dihedral angle of the initial value in the convergence criterion of 10^{-4} a.u.; the second step was to optimize the GaAs structures by using the result of the first step in the convergence criterion of 10^{-6} a.u.. Based on the optimized tubelike clusters, the unit cells of the infinite GaAsNTs were built by removing some atoms, and the same theory level was employed to optimize the repeated units with the periodic boundary condition calculations. All these calculations were implemented with the Gaussian 03 program package.[26]

3. Results and discussion

3.1. structures of $(GaAs)_n$ tubelike clusters

This work is aimed at a detailed study of the property evolution in tubelike $(GaAs)_n$ fullerenes. Taking the structures of $(GaAs)_n$ (n = 8, 12, 16, 20) as the basic framework, we stacked them along the central axis of the double-ring to form finite tubelike clusters. Then four stable tubular clusters with different section sizes have been obtained by full optimization. The growth behaviors of these tubelike cluster structures are shown in Fig. 1. From Fig. 1, one can find that all these structures contain two parallel polygons and p four-membered rings (on the wall of the tube) at the two ends, where p is the number of atoms for the

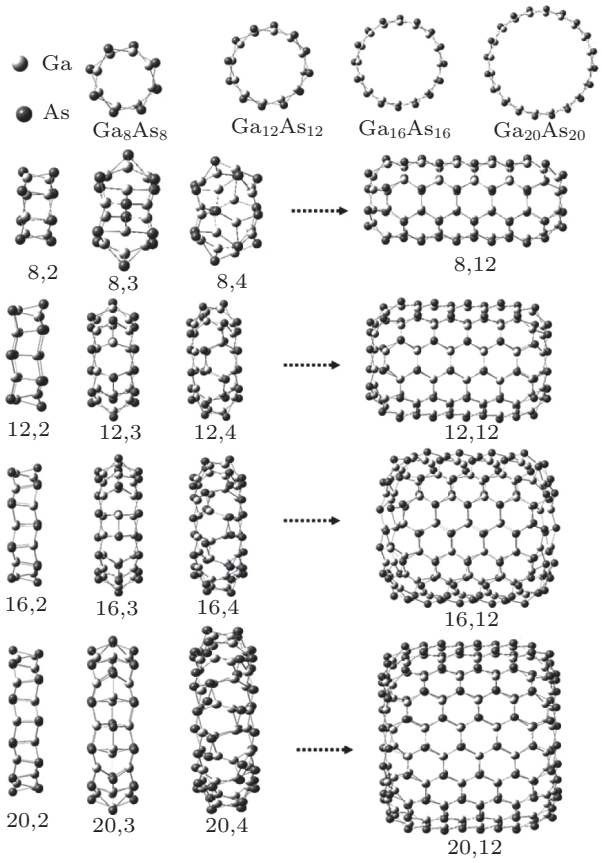


Fig. 1. Top view of the optimized $(GaAs)_n$ clusters (the first row; n = 8, 12, 16, 20) and side view of tubelike clusters $Ga_{pk/2}As_{pk/2}$ (all the rest; p = 8, 12, 16, 20; k = 2, 3, ..., 12).

polygon. Furthermore, on the assumption that k is the number of atomic layers in the structure, h, the quantity of the six-membered rings (6MRs) on the wall of the tube, can be inferred by

$$h = p(k-2)/2. \quad (1)$$

It means that for fixed p, the longer the tubelike cluster is, the more 6MRs there are. Meanwhile, for fixed k, the larger the diameter of the tubelike cluster is, the more 6MRs there are. Hence, we can conclude that 6MRs are the building blocks in the construction of tubelike clusters. According to these results, all the tubelike clusters in Fig. 1 can be classified by the common molecular formula, $Ga_{pk/2}As_{pk/2}$ or $Ga_{(p+k)}As_{(p+k)}$, where p is equal to 8, 12, 16, 20 and k ranges from 2 to 12. It is noteworthy that for $k > 3$ all of the structures have the point group S_p symmetry when it is even, while the $C_{ph/2}$ symmetry when it is odd.

Even though all the structures abide by some common rules, there are some differences in the structural parameters such as the Ga–As average length, the Ga–As–Ga angles, and the tube length for different p or k in the clusters. The mean bond lengths of the nearest neighbor Ga–As ($\bar{R}$), the bond angle of Ga–As–Ga ($\bar{\theta}$), and the total length of the cluster (L) are all listed in Table 1.

Table 1. Structural parameters of $(GaAs)_n$ $(8 \le n \le 120)$ tubelike clusters. Ga–As average bond length $\overline{R}$ in nm, the tube length (L) in nm, and the average Ga–As–Ga angle $\bar{\theta}$ in degree.

k	p=8			p=12			p=16			p=20		
	$\overline{R}$	L	$\bar{\theta}$	$\overline{R}$	L	$\bar{\theta}$	$\overline{R}$	L	$\bar{\theta}$	$\overline{R}$	L	$\bar{\theta}$
2	0.254	0.290	73	0.254	0.292	73	0.253	0.293	74	0.253	0.293	74
3	0.254	0.467	74	0.254	0.466	74	0.254	0.467	75	0.254	0.468	74
4	0.250	0.618	103	0.251	0.568	89	0.251	0.536	88	0.252	0.543	87
5	0.250	0.822	88	0.250	0.745	88	0.250	0.682	87	0.251	0.630	87
6	0.248	1.058	97	0.248	0.948	98	0.249	0.849	97	0.249	0.767	96
7	0.249	1.289	94	0.248	1.160	95	0.249	1.039	91	0.249	0.945	94
8	0.248	1.443	100	0.247	1.369	102	0.248	1.273	100	0.248	1.271	101
9	0.248	1.671	97	0.247	1.575	99	0.247	1.480	99	0.247	1.480	99
10	0.248	1.850	103	0.247	1.780	104	0.247	1.687	104	0.247	1.580	104
11	0.248	2.056	99	0.247	1.984	101	0.247	1.893	102	0.246	1.787	102
12	0.247	2.259	103	0.247	2.190	105	0.247	2.111	104	0.246	1.946	105

As shown in Table 1, for a determinate number of k, $\bar{R}$ and $\bar{\theta}$ with different p do not have great changes. When the number of layers is $k \ge 5$, the order of the total length L is $L\ (p = 8) > L(p = 12) > L(p = 16) > L(p = 20)$, which may be caused by the boundary effect. Moreover, the mean angle of Ga–As–Ga in the structures is all about 0.247 nm, which is very close to the 0.245 nm of the length in GaAs crystal.[27]

3.2. Size dependence of structural stability and electronic properties

Based on the optimized tubelike structures of $(GaAs)_n$ cluters, the average binding energy (E_b) is calculated to measure the relative stability of the clusters as well as the influence of the length and width. E_b is defined as the energy gained in assembling the $Ga_{pk/2}As_{pk/2}$ clusters from their isolated constituent atoms. It can be calculated by

$$E_b(k) = \frac{\frac{pk}{2}E_t(Ga) + \frac{pk}{2}E_t(As) - E_t(Ga_{pk/2}As_{pk/2})}{pk}$$
$$(p = 8, 12, 16, 20;\ k = 2, 3, \ldots, 12) \quad (2)$$

where $E_t(Ga)$, $E_t(As)$, and $E_t(Ga_{pk/2}As_{pk/2})$ represent the total energies of Ga atom, As atom, and $Ga_{pk/2}As_{pk/2}$ clusters, respectively. Figure 2 shows the binding energy $E_b(k)$ as a function of size k. We can see that the binding energy of the tubelike cluster increases gradually as the length increases for a certain p. This correlation indicates that the cluster becomes more stable as it becomes longer. However, the binding energy of the longest cluster is close to that of the GaAs bulk state (3.370 eV[28]). It is well known that 6MR is the most frequent structural motif in an immense variety of bulk III–V compound materials.[29] The optimized structures in this paper also possess

the same structural motif. When the tubelike cluster becomes longer, the number of 6MRs h will increase. Hence, the increase of h may be beneficial for the tubes' stability. On the other hand, the stabilities of the tubes do not depend linearly on the tubes' radii, which are represented by p. Furthermore, for all kinds of tubes (with different p), there is a transition of the curves at $k = 4$, where the proportion between p and h is 1:1, i.e., the number of 4MRs is equal to that of 6MRs in the structures. When $k \leq 4$, the proportion of $p : h$ is less than 1 and the slope of the curve is abrupt, whereas starting from k=5, the proportion of $p : h$ is beyond 1 and the ascending tendency of the curve becomes smooth. This may further verify that the content of 6MRs in the structures will affect the stability of the tube. Note that the binding energies of TLCP8, TLCP12, TLCP16, and TLCP20 almost overlap each other when $k \geq 10$, which indicates that their stabilities are similar. This similarity could arise from their similar structural parameters, like bond length (about 0.250 nm) and Ga–As–Ga bond angle (about 100°). To understand the electronic properties of these tubelike clusters, the size-dependent highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy gaps ($E_{\rm g}$), Fermi energy ($E_{\rm F}$), and some energy levels of nearby frontier orbits are calculated and plotted in Fig. 3. The $E_{\rm g}$ and $E_{\rm F}$ are respectively defined as

$$\begin{aligned} E_{\rm g} &= E_{\rm LUMO} - E_{\rm HOMO}, \\ E_{\rm F} &= E_{\rm HOMO} + (E_{\rm LUMO} - E_{\rm HOMO})/2, \end{aligned} \quad (3)$$

where the $E_{\rm HOMO}$ represents the energy of the highest occupied molecular orbital, and the $E_{\rm LUMO}$ is the energy of the lowest unoccupied molecular orbital. As shown in Fig. 3, when the layer of k increases, the distance between the neighboring energy levels decreases, and the energy levels are gradually approaching the level of $E_{\rm HOMO}$ or $E_{\rm LUMO}$. In addition, for all sorts of the tubes, there exists an obvious HOMO–LUMO energy gap, and the Fermi energy $E_{\rm F}$ is all around a constant of −5.2 eV. Thereby, the stability of the tubelike clusters may be attributed to the corresponding larger $E_{\rm b}$ and $E_{\rm g}$. In Fig. 3, one can also find that there are some differences in the electronic structures among these various tubes. As shown in Fig. 3(a), with the increase of the length there is a stair-like gradual increase in the energy gaps between HOMO–LUMO, while for all the other tubes there is also an obvious transition at $k = 4$ resembling their $E_{\rm b}$. When $k > 4$, the trends are different, and there is a stair-like gradual increase in the $E_{\rm g}$, yet as for TLCP8 the curve of gaps almost approaches a horizontal line with a small oscillation behavior. The large HOMO–LUMO energy gap for all of them ranging from 1.8 eV to 2.3 eV shows their semiconductor characteristics in common.

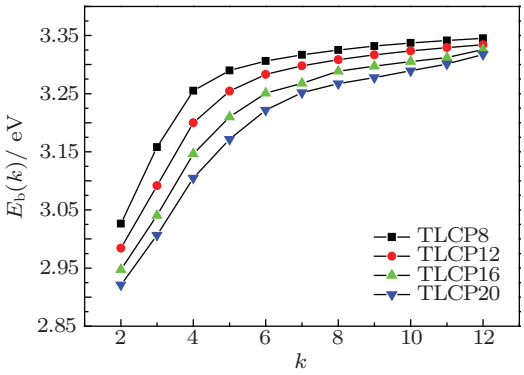


Fig. 2. (color online) Average binding energy of the clusters $(GaAs)_n$ as a function of size k.

In addition, we have generated the HOMO and LUMO molecular orbital surfaces for all of the tubelike clusters. To take the surfaces of TLCP8 and TLCP16 as examples, Fig. 4 shows that the main components of HOMO and LUMO come from 4p-orbital of Ga and As atom. In the case of the HOMO of all the tubelike clusters, the As p-orbital forms a π-bond with the Ga p-orbital. Even though there are some differences in both HOMO and LUMO among these various tubes, the characteristics of changes in common can be summarized as follows: with the tubes' length increasing, the HOMO and LUMO gradually transfer from the central toward the two terminals of the structure. The electron density distributions of HOMO and LUMO indicate that the chemical activity of the tubelike clusters at the two ends are stronger, which is propitious for the clusters to grow longer. That is why we can successfully attain the long stable tubelike clusters. Although the tubelike clusters are different in size, all of them are one-dimensional nanostructures. It is supposed that these one-dimensional nanostructures have the same microscopic growth mechanism: the chemical activities of the tubes at the two ends are stronger, which is propitious for the system to grow longer in one dimension. In fact, using the frontier molecular orbital theory to study the growth behavior of clusters is a simple and effective method, which have been developed into an optimum valence bond scheme.[30]

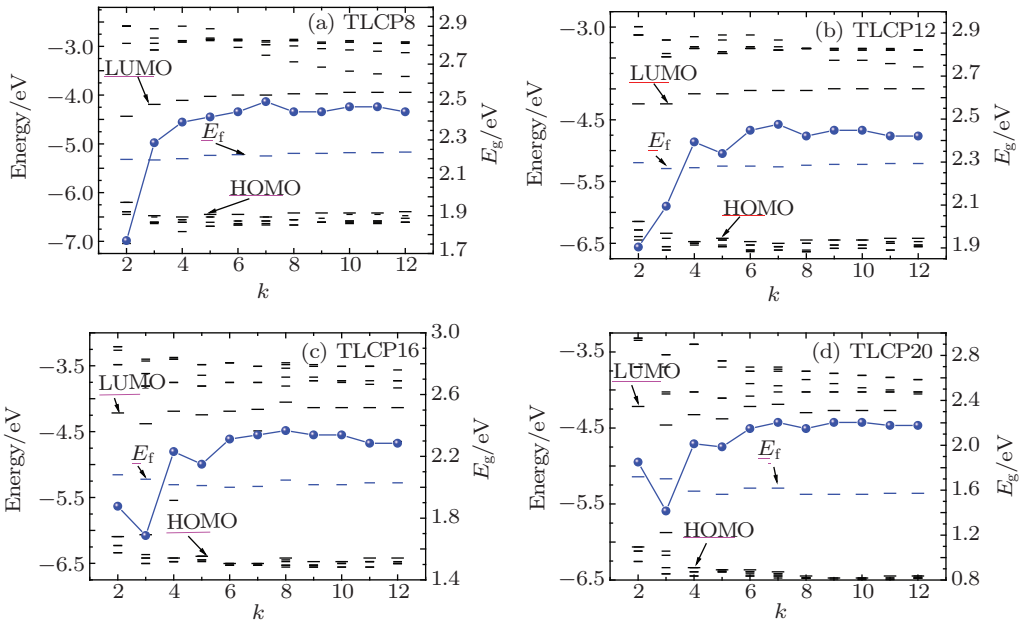


Fig. 3. (color online) Energy gaps, Fermi energies, and energy levels nearby frontier orbital of $(GaAs)_n$ tubelike clusters. The energy levels of nearby frontier obitals are HOMO-5, ..., HOMO-1, HOMO, LUMO, LUMO+1, ..., LUMO+6.

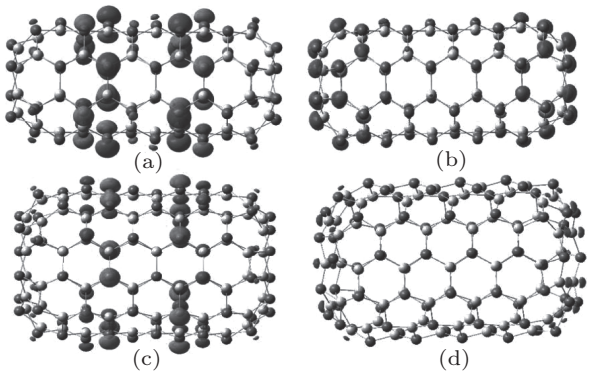


Fig. 4. The frontier molecular orbital surfaces of the HOMO of TLCP8 ($k = 12$) (a), the LUMO of TLCP8 ($k = 12$) (b), the HOMO of TLCP12 ($k = 12$) (c), and the LUMO of TLCP12 ($k = 12$) (d).

Table 2. Average on-site charges on Ga atoms in $(GaAs)_n$ ($8 \le n \le 120$) clusters.

k	$p = 8$	$p = 12$	$p = 16$	$p = 20$
2	0.261	0.290	0.308	0.318
3	0.276	0.298	0.312	0.324
4	0.306	0.318	0.323	0.325
5	0.321	0.336	0.337	0.340
6	0.329	0.348	0.352	0.351
7	0.335	0.356	0.286	0.362
8	0.339	0.361	0.367	0.400
9	0.339	0.366	0.373	0.378
10	0.346	0.369	0.378	0.382
11	0.348	0.370	0.381	0.386
12	0.351	0.374	0.396	0.389

As for bonding characteristics of the clusters, Mulliken population analysis[31] is conducted, and the average on-site charges on Ga atoms are all listed in Table 2. One can see that for a determinate number of k, the charge grows larger with the increase of p. It means that the charge transferring from Ga to As increases with the broadening of the tube radius. Furthermore, the increase of the on-site charge leads to an increase of ionicity of the clusters. When p is fixed the charge begins to increase with the increasing number of the layers k.

3.3. Infinite GaAsNTs

The increasing stability of the tubelike clusters with an increase of the number of layers k allows us to examine further the stability of the corresponding infinite nanotubes with a stoichiometric $(GaAs)_n$. These infinite nanotubes (GaAsNT) are built from homologous tubelike $Ga_{pk/2}As_{pk/2}$ ($k = 4$) clusters with a removal of two parallel polygons at the two ends of the structures to form the corresponding repeated units. These units, with a wire axis lying in the center, can be repeated by a translation vector along the axis. The values of the translation vectors are given by 0.8173 nm, 0.8205 nm, 0.8222 nm, and 0.8234 nm for GaAsNTP8 ($p = 8$), GaAsNTP12 ($p = 12$), GaAsNTP16 ($p = 16$), and GaAsNTP20 ($p = 20$), respectively. All of these structures have 6MR organizational units in common. Full structural relaxation

indicates that the infinite GaAsNTs have similar geometric structures with finite tubelike clusters, but some structural parameters have slight changes. The binding energies of the infinite tubes shown in Fig. 5 are slightly larger than those of the finite tubelike clusters, which means that it is possible to synthesize tubes long enough. It should be mentioned that the binding energy of NTP16 is larger than those of the other tubes with different sizes, while that of NTP8 is smaller, which is different from the case of tubelike clusters.

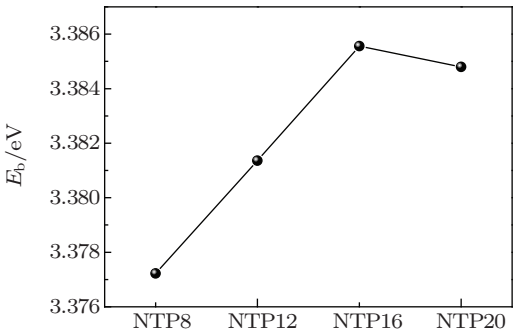


Fig. 5. Binding energy of infinite GaAsNTs including NTP8, NTP12, NTP16, and NTP20.

As for the electronic energy band structures of GaAs nanotubes, Fig. 6 indicates that the five-band structures clearly show the finite gap, the widths of which are 2.586 eV for Fig. 6(a), 2.484 eV for Fig. 6(b), 2.395 eV for Fig. 6(c), and 2.326 eV for Fig. 6(d). This implies that these nanotubes are direct wide gap semiconductors. In fact, all of these gaps are a lot larger than that of the GaAs bulk state (1.424 eV).[32] however, compared with HOMO–LUMO energy gap widths of the tubelike clusters as shown in Fig. 3, there are no essential changes for the similar structures. These results present a good way to adjust the gap width by forming different nanostructures. In order to further explain that the different structures will have different electrical conductinities, comparisons are made with the hybrid density functional study of armchair SiC single-walled nanotubes.[33] In the study, a single walled type (4,4) SiC nanotube corresponding to NTP8 has narrower tube diameters (0.702 nm) than NTP8 (1.062 nm), and a larger band gap (2.889 eV) than NTP8 (2.203 eV).

In order to further discuss the bond structure of the nanotubes, the density of states (DOS), the partial density of states (PDOS), and the crystal orbital overlap population (COOP) have been calculated, and the results are shown in Figs. 7 and 8. For the DOS of the nanotubes, within the energy range from −4.00 eV to −1.00 eV, the distributions of DOS are more diffuse, which means the π-bond is formed. Within the energy range from −8.00 eV to −5.00 eV, the distributions of DOS are more local, which means the σ-bond is formed. The PDOS shows that the main components of HOMO and LUMO come from 4*p*-orbital of Ga and As atoms. In the case of the HOMO of all the nanotubes, As *p*-orbital forms a π-bond with Ga *p*-orbital, which is consistent with the previous discussion on the tubelike clusters.

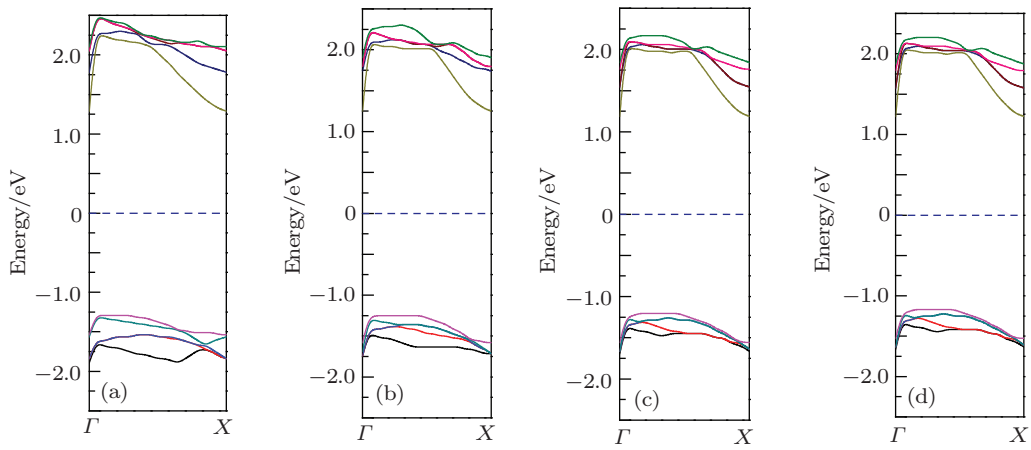


Fig. 6. (color online) Energy band structures (dispersion along Γ–X direction of the Brillouin zone) of the four sorts of GaAsNTs. (a) NTP8, (b) NTP12, (c) NTP16, (d) NTP20. The Fermi level indicated by the horizontal dashed line is set to be zero.

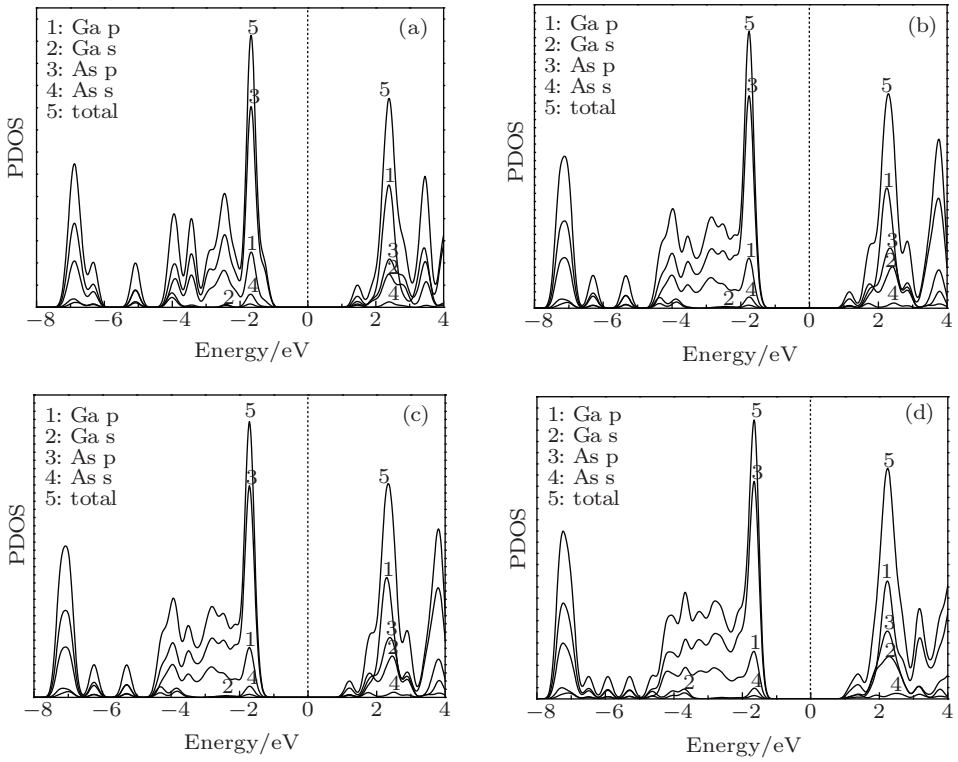


Fig. 7. The DOS and PDOS of infinite GaAsNTs including (a) NTP8, (b) NTP12, (c) NTP16, and (d) NTP20.

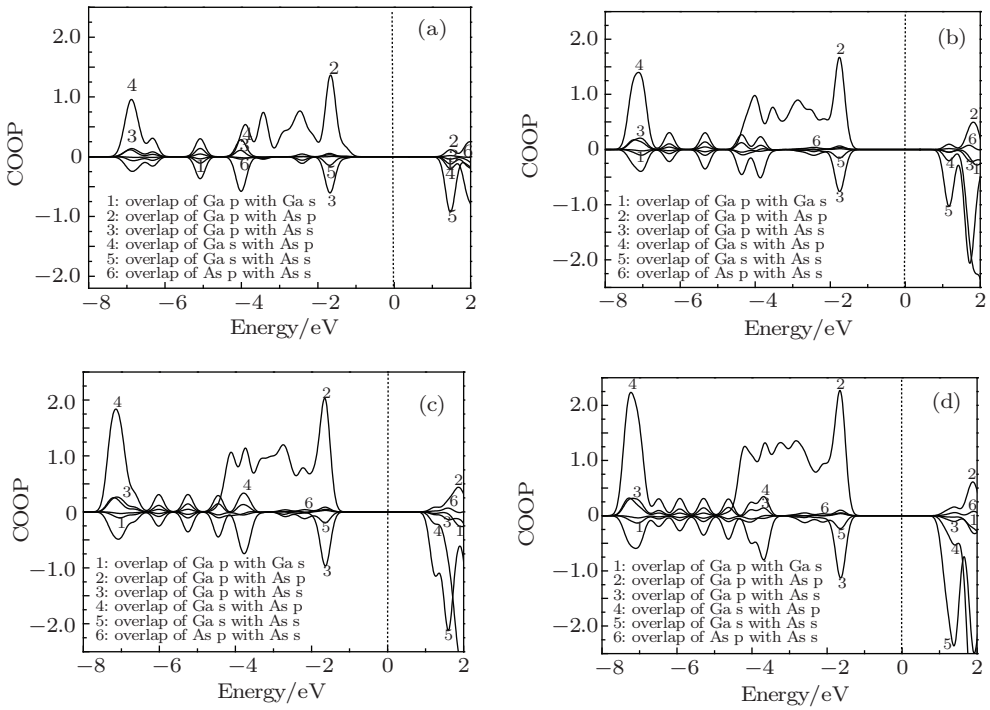


Fig. 8. The COOP of infinite GaAsNTs including (a) NTP8, (b) NTP12, (c) NTP16, and (d) NTP20.

As shown in the COOP in Fig. 8, within the energy range from −4.00 eV to −1.00 eV, the orbital overlap populations are more diffuse. Within the energy range from −8.00 eV to −5.00 eV, the orbital overlap population are more local. This is consistent with the previous discussion on the DOS.

From the COOP, most of the p-orbital electrons of Ga and As atoms filling the bonding orbital form the π-bond. The s-orbital electrons of Ga and As atoms, and the partial p-orbital electrons with partial s-electrons filled in the antibonding orbital form the σ^*-bond.

4. Conclusions

This paper reports the results of an investigation of GaAs tubelike clusters and infinite GaAsNTs. The different properties of the optimized tubelike clusters and nanotubes, such as the structures, binding energy, Mulliken charge population, HOMO–LUMO energy gaps, frontier molecular orbital surface, energy band structures, density of states, the partial density of states, and the crystal orbital overlap population were analyzed. Based on the results, several points can be summarized as follows.

(i) A family of stable tubelike $(GaAs)_n$ clusters are observed when $n \geq 8$. The molecular formula of these clusters can be classified as $Ga_{pk/2}As_{pk/2}$. During the growth process of the clusters, the two parallel polygons and p 4MRs should be considered as the skeleton of the structures, and 6MRs should be regarded as the building blocks.

(ii) The analysis of binding energies shows that when $p = 8$, the systems are more stable than other sizes for both of the tubelike clusters and the infinite nanotubes. The finite tubes have large HOMO–LUMO energy gaps. In addition, the electron density distributions of HOMO and LUMO indicate that the chemical activity of the tubelike clusters at the two ends is strong, which is conductive for the clusters to grow longer.

(iii) The infinite GaAsNTs have similar geometric structures to the finite tubelike clusters and present wide gap semiconductivity due to their large band gaps. In GaAsNTs, most p-orbital electrons of Ga and As atoms filling the bonding orbital form the π-bond. The s-orbital electrons of Ga and As atoms, and partial p-orbital electrons with partial s-electrons filling the antibonding orbital form the σ^*-bond.

References

[1] Dobrowolski W, Kossut J and Story T 2003 *Handb. Magn. Mater.* **15** 289

[2] Kamat P V 1993 *Chem. Rev.* **93** 267

[3] Cox S D, Gier T E, Stucky G D and Bierlein J J 1988 *J. Am. Chem. Soc.* **110** 2986

[4] Wang Y and Herron N J 1988 *J. Phys. Chem.* **92** 4988

[5] Cooke M 2006 *III–Vs Rev.* **19** 18

[6] Dong J R, Yang H, Tian C, Huang J and Zhang H Y 2012 *Chin. Phys.* B **21** 067303

[7] Ge J, Liu H G, Su Y B, Cao Y X and Jin Z 2012 *Chin. Phys.* B **21** 058501

[8] Chen L, Qian Y S, Zhang Y J and Chang B K 2012 *Chin. Phys.* B **21** 034214

[9] Gu L Y, Li Y F, Chu W D and Wei Y H 2012 *Chin. Phys.* B **21** 037301

[10] Patriarche G, Glas F, Tchernycheva M, Sartel C, Largeau L, Harmand J C and Cirlin G E 2008 *Nano. Lett.* **8** 1638

[11] Song B and Cao P L 2002 *Phys. Lett.* A **300** 485

[12] Gutsev G L, Oneal R H, Saha B C, Mochena M D, Johnson E and Bauschlicher C W Jr 2008 *J. Phys. Chem.* A **112** 10728

[13] Qu Y H, Ma W Y, Bian X F, Tang H W and Tian W X 2005 *J. Mol. Graph. Model* **24** 167

[14] Goldberger J, He R, Zhang Y, Lee S, Choi H J and Yang P 2003 *Nature* **422** 599

[15] Xu Z, Golberg D and Bandoa Y 2009 *Chem. Phys. Lett.* **480** 110

[16] Guo Y H, Yan X H and Yang Y R 2009 *Phys. Lett.* A **373** 367

[17] Karamanis P, Carbonniere P and Pouchan C 2009 *Phys. Rev.* A **80** 053201

[18] Gutsev G L, Johnson E, Mochena M D and Bauschlicher C W Jr 2008 *J. Chem. Phys.* **128** 144707

[19] Ghosh C, Pal S, Goswami B and Sarkar P 2007 *J. Phys. Chem.* C **111** 12284

[20] Sarkar P and Springborg M 2003 *Phys. Rev.* B **68** 235409

[21] Ghosh C, Pal S, Goswami B and Sarkar P 2005 *Chem. Phys. Lett.* **407** 498

[22] Brena B and Ojamae L 2008 *J. Phys. Chem.* C **112** 13516

[23] Becke A D 1988 *Phys. Rev.* A **38** 3098

[24] Lee C, Yang W and Parr R G 1988 *Phys. Rev.* B **37** 785

[25] Wadt W R and Hay P J 1985 *J. Chem. Phys.* **82** 284

[26] Frisch M J, Trucks G W, Schlegel H B, *et al.* 2004 *Gaussian* 03, Revision B.03 Gaussian Inc.: Wallingford CT

[27] Stevenson A W 1994 *Acta Crystallographica* A **50** 621

[28] Zhao J J, Xie R H, Zhou X L, Chen X S and Lu W 2006 *Phys. Rev.* B **74** 035319

[29] Zhang S L, Zhang Y H, Huang S P, Liu H and Tian H P 2010 *Chem. Phys. Lett.* **498** 172

[30] Shen X Y, Xu Y G, He C L, Liu H T and Li J M 2005 *Eur. Phys. J.* D **34** 109

[31] Mulliken R S 1955 *J. Chem. Phys.* **23** 1841

[32] Chen Q S 2010 "The First Principles Study of GaAs'optical Properties and Electricity Properties" (MS Thesis) (Xian: Xidian University) (in Chinese)

[33] Alam K M and Ray A K 2008 *Phys. Rev.* B **77** 035436