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ARTICLE *in* JOURNAL OF MOLECULAR MODELING · MARCH 2014

Impact Factor: 1.74 · DOI: 10.1007/s00894-014-2171-2 · Source: PubMed

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ORIGINAL PAPER

Ab-initio study of structural, electronic, and transport properties of zigzag GaP nanotubes

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Received: 12 September 2013 / Accepted: 4 February 2014

Abstract Stability and electronic properties of zigzag ($3 \leq n \leq 16$) gallium phosphide nanotubes (GaP NTs) have been analyzed by employing a systematic ab-intio approach based on density functional theory using generalized gradient approximation with revised Perdew Burke Ernzerhoff type parameterization. Diameter dependence of bond length, buckling, binding energy, and band gap has been investigated and the analysis shows that the bond length and buckling decreases with increasing diameter of the tube, highest binding energy of (16, 0) confirms this as the most stable amongst all the NTs taken into consideration. The present GaP NTs shows direct band gap and it increases with diameter of the tubes. Using a two probe model for (4, 0) NT the I-V relationship shows an exponential increase in current on applying bias voltage beyond 1.73 volt.

Keywords Ab-initio · Band structure · Buckling · GaP · I-V curve · Nanotubes

Introduction

Since the discovery of carbon nanotube (CNT) [1, 2], in 1991-93, numerous theoretical and experimental effects have been devoted to explore the one dimensional tubular material and its possible applications. A CNT can be thought of as a seamless cylinder formed by rolling up a graphene sheet. The properties of CNT are derived by its geometry, which depends upon tube diameter and its chiral (twisting) angle. Promising applications of CNTs in the field of electronics, medical, thermal, optical, mechanical, and in other industries [3–8] have motivated a number of investigations on the possibility of other nanotubes; where inorganic semiconducting compounds have attracted a lot of researchers with the first report on WS_2 nanotubes in 1991 itself [9]. A number of stable nanotubes of different inorganic semiconductors such as GaN, BN, and InN have been predicted theoretically and synthesized successfully as reported elsewhere [10–16]. Gallium phosphide (GaP) is a popular semiconductor with a wide band gap of 2.26 eV [17], and is found to be an important candidate for light emitting particularly in the visible range. Literature shows that one dimensional GaP nano wires and nano tubes have emerged as an interesting candidate to be explored. GaP nanowires have been synthesized through different preparation routes [18, 19]. Recently Wu et al. have reported the successful synthesis of polycrystalline GaP NTs possess zinc blend structure with unique optical properties due to intrinsic semiconducting behavior [20]. Another group reported the NMR properties of armchair and zigzag GaP NTs based on density functional theory and found that armchair GaP NTs could be considered as a more reactive material than zigzag NTs to interact with other atoms or molecules [21]. However not much literature is available on these III-V NTs, hence more research is needed to find the promising application of GaP NTs by characterizing its properties, a reason for selecting the present piece of work analyzing the stability and electronic properties of Zigzag single wall GaP NTs over a range $3 \leq n \leq 16$. Our group has recently reported the structural and electronic properties of a variety of nanostructures like nanowires, CNTs as well as III-V NTs [22–28] using first principle approach. Where, we have reported the geometry as

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Published online: 02 March 2014

well as diameter dependence of electronic properties of nanowires [22, 23], single walled BN, BP, BAs, GaAs, GaN NTs [24, 25], and recently analysis of defect and strain induced variation in CNTs [26–28].

The present study analyzes the stability and diameter dependence of band gap of GaP NTs and also reports the transport behavior in a two probe model of (4, 0) GaP NT. In the next section computational method has been discussed briefly followed by results and discussion.

Computational methodology

The present theoretical analysis has been performed using the density functional theory (DFT) [29, 30] and non-equilibrium Green function (NEGF) [31] based ab-initio code named Atomistix Toolkit (ATK-VNL) [32]. ATK-VNL is a further development of TranSIESTA-C [33] and is based on the methodology, models, algorithms developed in academic code TransSIESTA and in part, McDCal [34], employing localized basis sets as developed in SIESTA [35]. The generalized gradient approximation with revised Perdew Burke Ernzerhoff [36, 37] type parameterization has been utilized for exchange correlation energies. Where, valence electrons were described by localized pseudo atomic orbital's (PAOs) [38], with double-ζ double polarized basis set [35]. A large plane wave mesh cut-off of 150Ryd is used throughout the calculation. k-point sampling of 1×1×20 has been used for achieving the total energy convergence to investigate the structural and electronic properties. In full course of optimization, the run was performed with maximum force tolerance set at 0.05 eV/Å.

Results and discussion

Stability analysis

The present work carries the specific objective of investigating the diameter dependence of the structural and electronic properties of optimized (n, 0) zigzag single walled GaP NTs (3≤n≤16). To analyze the stability, we have computed the equilibrium bond length for different sized NTs through total energy minimization as reported in Table 1. In our findings a continuous decrement in the bond length ranges from 2.37 to 2.24 Å, has been observed for 3≤n≤10 NTs and then became constant for NTs with 10≤n≤16. The average computed Ga-P bond length is 2.26 Å, which is very close to that reported by Mirzaei et al. [21]. On optimizing the geometry, the tube surface gets buckled, this is because more electronegative atoms (P atoms) moved radially outward and more electropositive atoms (Ga atoms) have been displaced inward as shown in Fig. 1. The buckled tube contains only one type of atom on each edge, similar to that observed in other inorganic nanotubes [39, 40].

Table 1 Diameter, binding energies and total energy of GaP NTs (3≤n≤16)

Chirality (n, m)	No. of atoms (N)	Bond length (Å)	Diameter (Å)	Binding energy (E_b) (eV)	Total energy (E_T) (eV)
(3,0)	12	2.37	3.92	3.802	−1950.87
(4,0)	16	2.29	5.05	4.012	−2604.52
(5,0)	20	2.27	6.26	4.141	−3258.22
(6,0)	24	2.26	7.48	4.203	−3911.36
(7,0)	28	2.26	8.72	4.247	−4564.22
(8,0)	32	2.25	9.92	4.261	−5216.99
(9,0)	36	2.25	11.16	4.276	−5869.67
(10,0)	40	2.24	12.35	4.287	−6522.29
(11,0)	44	2.24	13.58	4.295	−7174.87
(12,0)	48	2.24	14.81	4.305	−7827.43
(13,0)	52	2.24	16.05	4.311	−8479.97
(14,0)	56	2.24	17.28	4.312	−9132.44
(15,0)	60	2.24	18.52	4.313	−9784.97
(16,0)	64	2.24	19.76	4.315	−10437.46

Tendency of buckling of these inorganic compound nanotubes is the result of distinct hybridization of two different atoms in curved hexagonal layer. However, the degree of buckling in these NTs reduces with increase in radius. Figure 2 shows the variation of buckling as a function of tube radius, that is calculated by subtracting mean radius of Ga atoms from mean radius of phosphorous atoms. The buckling vs tube radius plot also shows that (3, 0) GaP NT has the highest degree of buckling while (16, 0) the lowest, which means larger diameter tubes have less buckling. For further analyzing the stability of NTs, we have also calculated the binding energies of different NTs varying in terms of total number of atoms present and tube diameter by using the following relation:

$$E_b = [N E_T(Ga_{iso}) + M E_T(P_{iso}) - E_T(GaP\,SWNT)]/(N+M).$$

Where, E_T stands for the total energy considered for isolated Ga and As atoms along with GaP single wall nanotube (SWNT), N and M are the number of gallium and phosphorous atoms present in the tube respectively.

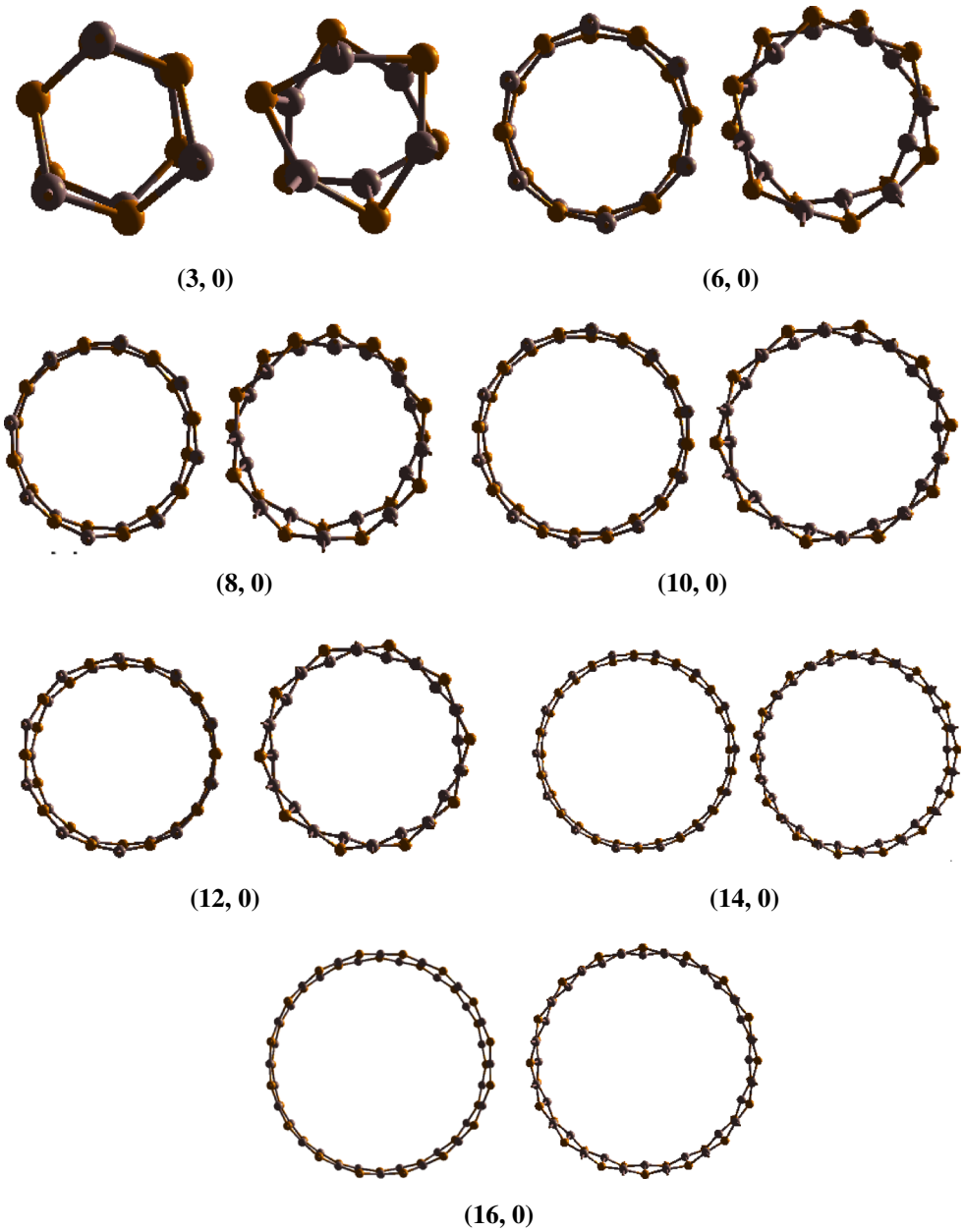


Fig. 1 Initial geometries and optimized geometries of GaP NTs

Table 1 reveals the dependency of binding energies on diameter, which continuously increase with the diameter of nanotube. Figure 3 shows that (3, 0) GaP NT has the lowest binding energy with the least number of atoms while the (16, 0) NT possess maximum binding energy with highest number of atoms. Nanotubes with lowest total energy and highest binding energy have been considered as the most stable amongst all the tubes taken into consideration. This analysis confirms that for larger diameter and number of atoms, stability of SWNTs increases.

Electronic properties

The electronic properties of optimized geometry of GaP SWNTs have been analyzed and calculated band gaps and Fermi energies for single walled GaP NTs are listed in Table 2 as a function of tube diameters and indices. The electronic band structure analysis shows that all the zigzag GaP NTs taken into consideration in the present work are found to be semiconducting and show direct band gap at Γ point. The analysis shows that the band gap increases with increasing the diameter for all the considered nanotubes, which is in

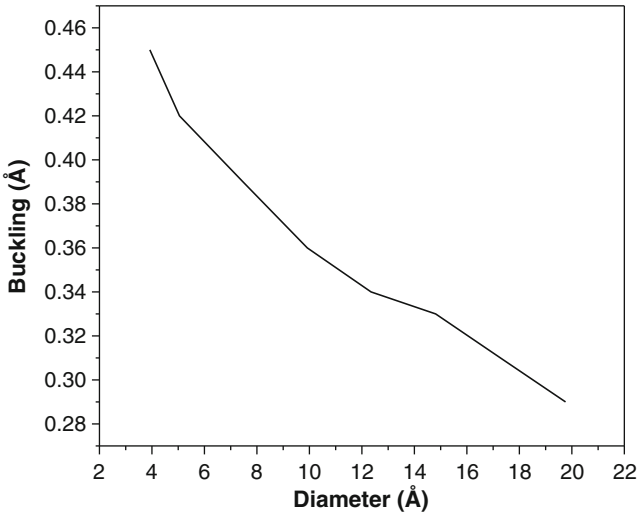


Fig. 2 Buckling as the function of tube diameter

Table 2 Band gap and Fermi level for GaP NTs

Chirality (n, m)	Band gap (eV)	Fermi energy (eV)
(3,0)	0.29	−4.90
(4,0)	0.62	−4.93
(5,0)	1.10	−4.66
(6,0)	1.50	−4.52
(7,0)	1.72	−4.47
(8,0)	1.83	−4.22
(9,0)	1.94	−4.45
(10,0)	2.02	−4.12
(11,0)	2.05	−3.92
(12,0)	2.12	−3.83
(13,0)	2.14	−4.07
(14,0)	2.15	−4.05
(15,0)	2.17	−3.89
(16,0)	2.20	−3.73

reasonable agreement with the results reported for the other III-V NTs [39–42]. However, the reason behind increment in band gap on increasing the diameter might be rehybridization of σ-JI orbitals which does not remain orthogonal to each other because of the curvature of tube. Another reason could be the strain, which also affects their electronic properties, which is higher in smaller diameter tubes, and on increasing tube diameter the strain band gap decreases as reported elsewhere [40, 41]. The analysis shows that (3, 0) GaP NTs is semiconducting with the lowest band gap of about 0.29 eV, and beyond that the band gap increases and reaches at 2.20 eV for (16, 0) SWNT. All the considered NTs have a band gap less than its bulk counterpart which is about 2.24 eV.

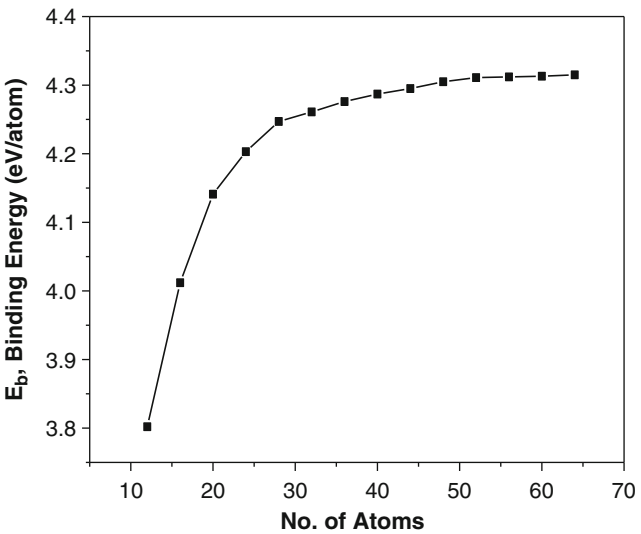


Fig. 3 Binding energy as a function of total number of atoms in GaP NTs

To further analyze the electronic structures of the GaP NTs, we have also calculated the density of states (DOS), where the lower part of the valance band is dominated by the 4s states of phosphorous, and its 4p electronic states present near the Fermi level have a key role in conduction, while Ga 4s states reside just between them. On the other hand Ga 4p states dominate in the conduction band. On observing DOS profiles for $3 \leq n \leq 16$ GaP NTs, no peak has been found at their Fermi level, evident of their semiconducting behavior, however dispersed peaks can be seen in conduction band and valance band with one of them reaching the maxima. The maximum peaks in conduction band for $3 \leq n \leq 16$ are present at around 6.66, 6.42, 8.24, 8.13, 8.77, 8.19, 8.10, 8.94, 7.78, 8.81, 9.72, 3.95, 3.69, 0.87 eV respectively, and the same in valance band at -0.27, -0.69, -1.05, -0.90, -0.87, -1.24, -6.76, -7.12, -7.32, -7.39, -7.18, -7.22, -7.38, -7.53 eV respectively. The band structures along with its DOS profile for GaP NTs are shown in Fig. 4.

Transport properties

The electronic properties computation performed in the present work finds the electronic band gap of (4, 0) in the range of widely used bulk germanium, however we thought it pertinent to investigate its transport properties too for its future device application. To analyze the transport properties of these NTs, a two probe model has been constructed using the optimized (4, 0) nanotube as shown in Fig. 5.

The above model can be divided into three parts, left semi infinite electrode, right semi infinite electrode, and central region. Central region constitutes the scattering region, left

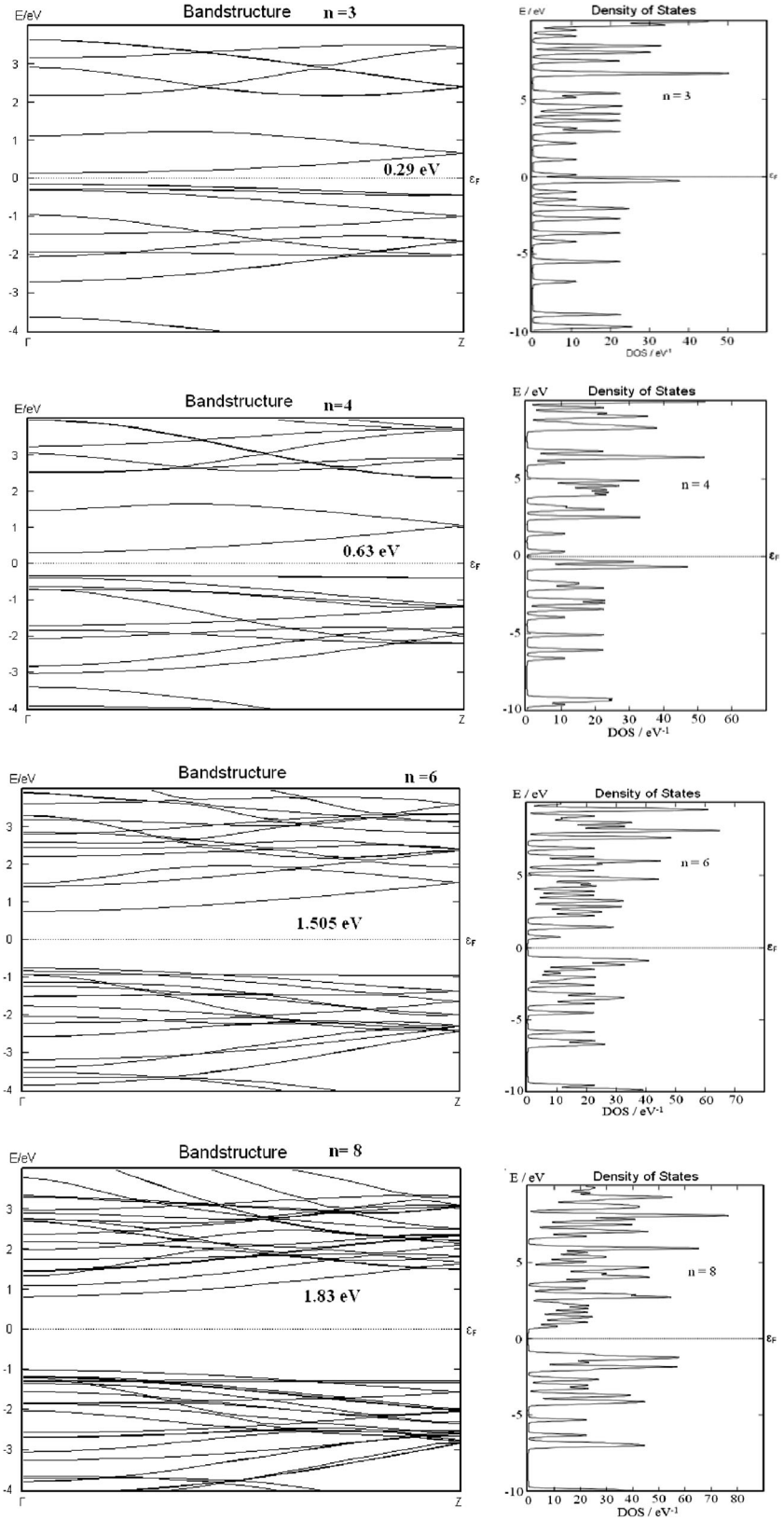


Fig. 4 Band structure and DOS of GaP NTs with n=3, 4, 6, 8, 10, 12, 14, and 16

and right electrode are extensions [43–45]. As all three regions are constituted through repeatation of (4, 0) GaP NT unit cell a large K point sampling of 1×1×100 has been used to calculate the transmission spectrum and I-V relationship. The current

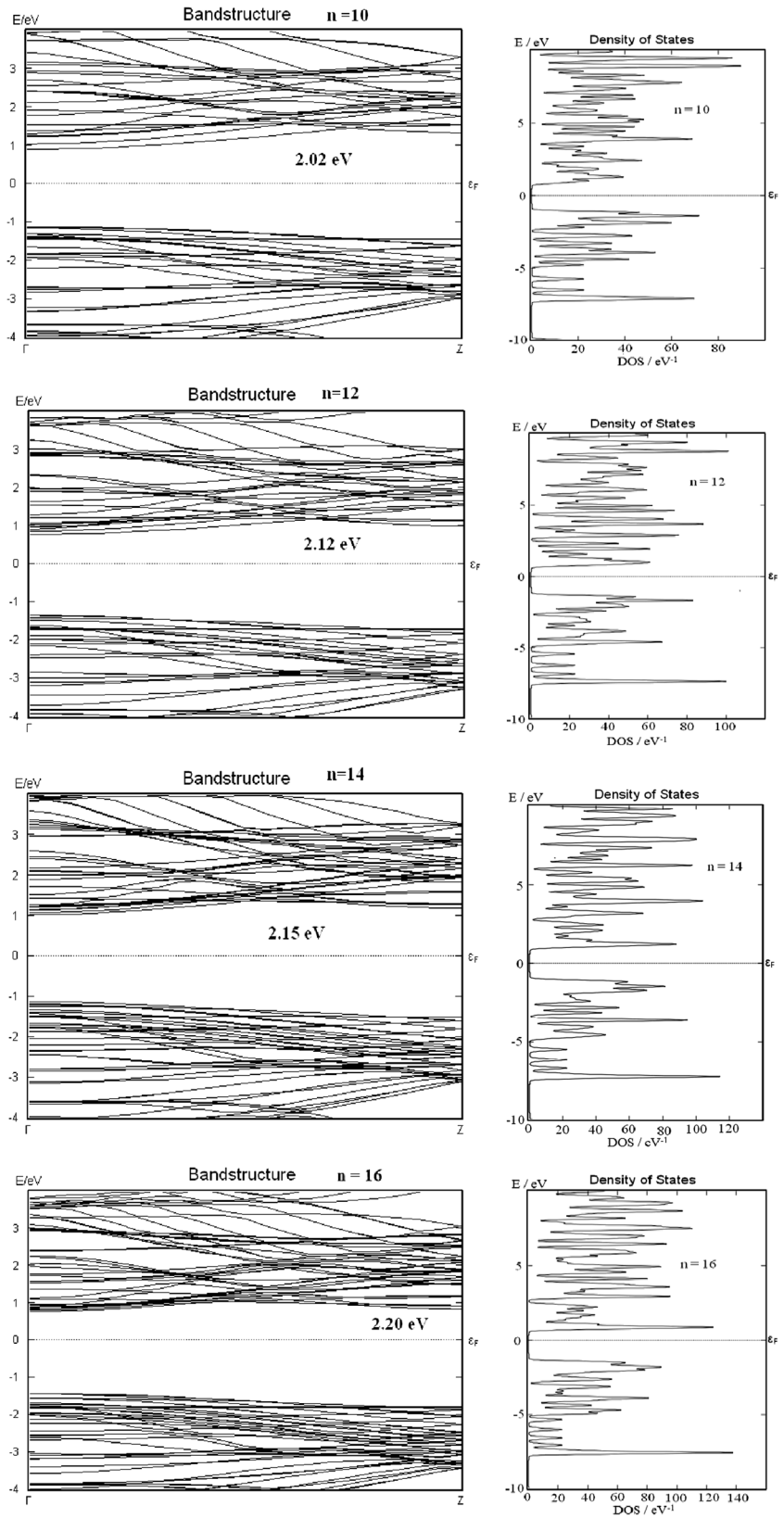


Fig. 4 (continued)

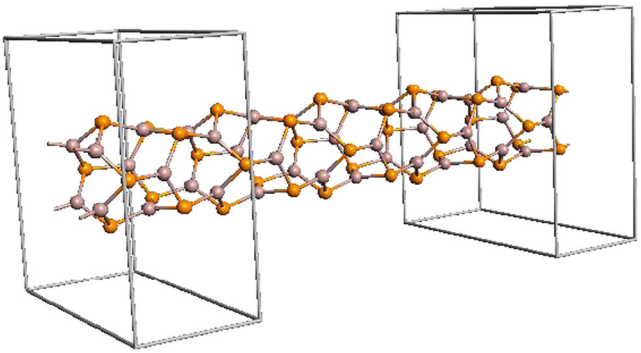


Fig. 5 Two probe model for (4, 0) GaP nanotube

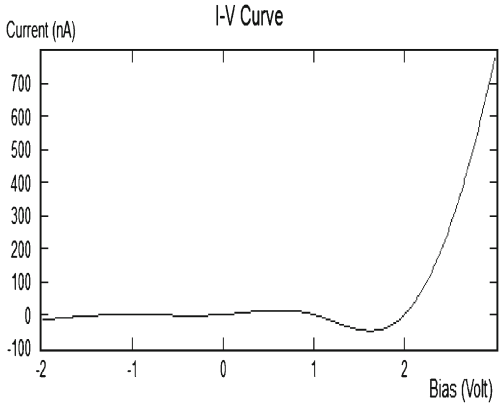


Fig. 7 Current-voltage characteristics of (4, 0) two probe model

through this system can be obtained from Landauer-Biittiker formula [46, 47].

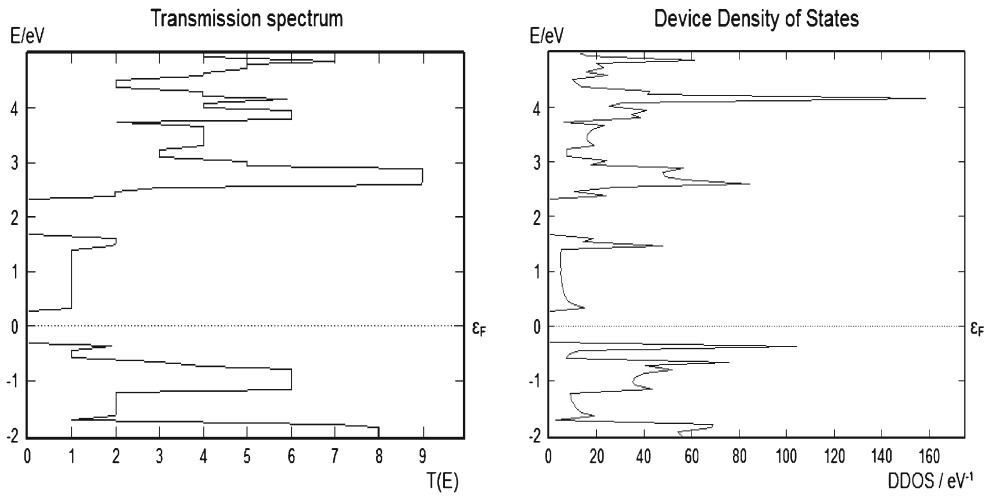
$$I = \frac{2e}{h}\int_{\mu_L}^{\mu_R}(T(E)[f_L(E) - f_R(E)])dE$$

Where, $\mu_{L(R)}$ is the chemical potential of left (right) electrode. $f_{L(R)}(E)=(\exp[(E-\mu_{L(R)})/K_BT]+1)^{-1}$ is the electronic Fermi distribution function for left (right) electrode. The transmission coefficient T(E) describes the probability of transmission of electrons between the electrodes with energy E and can be calculated using Green function [46] at bias voltage V as:

$$T(E) = T_r\left(\Gamma_L(E,V)G_c^{ret}(E,V)\Gamma_R(E,V)G_c^{adv}(E,V)\right).$$

Where, G_c^{ret} and G_c^{adv} are the retarded and advanced Green function of conductor, while $\Gamma_{L(R)}$ is the coupling matrices. Using the above discussed two probe model discussed above, the transmission spectrum and device density of states have been calculated at zero bias voltage to analyze the transport properties of the device. Figure 6 shows that the tansmission cofficient T(E) is zero at Fermi level which agrees with our electronic band structure results, here transmission gap exists atFermi level confirming the semiconducting nature of the tube. However dispersed peaks can be seen above and below the Fermi level, a similar characteristic as in device density of states. Maxima in device density of states has been observed at 4.15 eV and -0.37 eV above and below the Fermi level respectively. Transmission gap in spectra also confirms the probability of passing the electrons through the tube at almost zero, until the appropiate bias voltage is not applied. To analyze this effect we applied the biasing on electrode in the range -2 to 3 V shown in I-V curve (Fig. 7), where a negligible amount of current flow for bias voltage ranges from -2 to 1.7 V, and then on increases of the biasing beyond 1.73 V, current started to grow linearly which is obvious for semiconductor devices.

Fig. 6 Transmission spectra and DDOS for (4, 0) two probe model



Conclusion

The electronic band structures of zigzag (n,0) NTs with $3 \leq n \leq 16$ and transport properties of (4, 0) GaP NT were investigated by using ATK-VNL an ab-initio code based on density functional theory coupled with a non-equilibrium Green function approach. On optimizing the tube geometry a certain degree of buckling has been observed in tubes, the reason being a slight difference in hybridization of Ga and P atoms which is not the case in conventional CNTs. The magnitude of the buckling decreases for larger diameter tube, and calculated binding energies shows that stability of these NTs increases with increasing the diameter of tube. The band gap of nanotube increases with the increase in tube diameter. The electronic transport analysis of (4, 0) GaP NT shows no current flow up to 1.73 V bias voltage, and beyond that it grows linearly.

Acknowledgment The authors are thankful to ABV-IIITM, Gwalior for providing the infrastructural support to perform the present computation at Computational Nano science and Technology Lab.

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