I. INTRODUCTION

Carbon nanotubes are unique one dimensional nanostructures with their exceptional mechanical, electronic and magnetic properties. While the use of single-wall carbon nanotubes (SWCNT) requires a completely new paradigms in the development of nanodevices, Si still continues to attract interest for electronic applications in nanotechnology. Therefore, Si based nanotubes have been subject of experimental and theoretical analysis.

Even if a single-wall Si nanotube (SWSiNT) has never been observed, theoretical predictions have been performed for various kinds of Si tubes. Fagan et al. have investigated the structural and electronic properties of chiral SWSiNTs based on Density Functional Theory (DFT). Barnard et al. have examined the dependence of heat of formation and binding energy of SWSiNTs on their radius and chirality. The stability of (10,0) SWSiNT has been examined by using empirical Monte-Carlo molecular dynamics method and found that it is stable at finite temperature. Ivanovskaya et al. investigated hypothetical Si nanotubes containing regular chains of metallofullerenes using one dimensional tight-binding model within Hückel approximation. By using ab-initio calculations, Dumitrica et al. described how the smallest (2,2) and (3,0) SiNTs are stabilized by the axially placed metal atoms from different groups of periodic table. Ponomarenko et al. studied the energetics and relative stability of infinite and finite, clean and hydrogenated open-ended Si nanotubes by using the extended Brenner potential. The existence of H-doped stable tube-shaped finite SiNTs have been predicted and their electronic structures have been compared with those of carbon nanotubes. Seifert et al. have argued that structures of silicate and SiH nanotubes are more stable than bare Si nanotubes. Singh et al. have investigated the stability of finite and infinite hexagonal prismatic structures of Si with 3d magnetic elements and predicted that such structures can be stabilized through doping by the elements of transition metal (TM). Fullerene-structured Si tubulars, possibly based on Si_{24} have been produced. More recently, the successful synthesis of multiwalled Si nanotubes has been reported. Now, SWSiNTs are no longer hypothetical structures and it is not unrealistic to expect their fabrication with controllable size and diameter. Similarly, achievements of synthesis of single-wall BN nanotubes and GaN, AlN thick-wall tubular forms has increased the interest in the theoretical analysis of compound nanotubes.

In addition, the synthesis of Mo and W chalcogenid nanotubes, and also NiCl tubular and cage structures have been realized. In this paper we present a theoretical analysis of Si- and III-V compound nanotubes based on a state-of-the-art first-principle calculations. Our work is concentrated mainly on the tube structures which can be viewed as the rolling of graphene like honeycomb planes of Si or III-V elements on a cylinder of radius R. Starting from the precursor graphene-like honeycomb structures we investigated their stability, energetics and electronic properties of these nanotubes. Since O, O_{2}, Si, Au and H are critical elements for various processes on Si, we also examined the adsorption of these atoms on SWSiNT. Finally, we studied the stabilization of unstable, small-diameter SWSiNTs through the internal and external adsorption of transition metal elements. In addition, we found that
tubular structures which are generated by stacking of triangles, pentagons and hexagons of Si are stable and metallic. The (8,0) zigzag tubes of AlP, GaN and GaAs are stable and semiconducting. The results obtained from the present study have been compared systematically with those of SWCNT. The stable tube structure predicted in this study are hoped to motivate experimental research aiming at the synthesis of various tubular structures of group IV elements and III-V and II-VI compounds.

II. METHOD

We have performed first-principles plane wave calculations\[30, 31\] within DFT\[32\] using ultra-soft pseudopotentials.\[31, 33\] The exchange correlation potential has been approximated by Generalized Gradient Approximation. (GGA)\[34\] Structures incorporating TM atoms have been calculated using spin-polarized GGA. For partial occupancies we use Methfessel-Paxton smearing method.\[37\] The width of smearing is chosen between 0.01-0.1 eV depending on the system. All structures have been treated by supercell geometry using the periodic boundary conditions. To prevent interactions between adjacent structures a large spacing (~ 10 Å) has been taken. Convergence with respect to the number of plane waves used in expanding Bloch functions and k-points in sampling the Brillouin zone are tested for the parent bulk crystals as well as tubular structures. In the self-consistent potential and total energy calculations Brillouin zone of nanotubes has been sampled by (1x1x19) mesh points in k-space within Monkhorst-Pack scheme.\[36\] Calculations of graphene and graphite structures have been carried out using (19x19x1) and (8x8x6) k-point samplings, respectively. A plane-wave basis set with kinetic energy cutoff 200 eV ≤ ℏ^2|k| + G|G|^2/2m ≤ 330 eV has been used. All atomic positions and lattice parameters are optimized by using conjugate gradient method where total energy and atomic forces are minimized. The convergence for energy is chosen as 10^-5 eV between two ionic step, and the maximum force allowed on each atoms is 0.05 eV/Å.

It should be noted that DFT based methods provide reliable predictions for the ground state properties, but band gaps are usually underestimated. Hence the energy band structure obtained from the single particle energy eigenvalues of Kohn-Sham equations are only approximations to the real energy bands. Proper many-body self-energy corrections can be made by using GW method.\[37\] Recently, GW energies are compared with DFT-LDA results of (n,0) SWCNTs which indicates shifts of valence and conduction bands and considerable increase of LDA band gap from 0.2 eV to 0.6 eV.\[38\] It is suggested that GW corrections are small for large radius SWCNTs. Performing first-principles many-body Green’s function calculations Spataru et al.\[39\] showed that the optical spectrum of both semiconducting and metallic small-radius SWCNTs exhibit important excitonic effects due to quasi-one dimensional nature. It is interesting to note that while the band gaps of (9,0), (12,0) and (15,0) zigzag SWCNTs have been measured by Scanning Tunneling Spectroscopy\[40\] to be 80, 42 and 29 meV, respectively, same band gaps have been predicted by GGA calculation\[41\] to be 93, 78 and 28 meV, respectively.

The stability of the structures we studied is the most crucial aspect of our work, since it provides valuable information for the synthesis of these materials in future. In this respect an extensive analysis of stability has been carried out for various nanotubes. First, we applied a radial deformation to certain nanotubes and optimized their structures to see whether they relax to their original, undeformed circular forms under zero external force. Furthermore, we have performed, finite temperature ab-initio molecular dynamics calculations up to 1000 K using Nosé thermostat\[42\] for 250 time steps (0.5 ps) to check whether the optimized structure will be affected from random thermal motion of atoms or they maintain their tubular form at high-temperature. We believe that if there were any kind of structural instability it would be initiated and also enhanced within these time-steps at high temperature.

III. HONEYCOMB STRUCTURE OF SILICON AND III-V COMPOUNDS

One of the main difficulties for synthesizing Si nanotubes seems to be the absence of 2D silicon layer similar to the graphene structure of carbon. This is traced to the fact that in contrast to carbon, \(sp^3\)-hybridization in Si is more stable than \(sp^2\)-hybridization.\[43\] In view of this situation we examined whether the graphene-like 2D sheet of silicon can be stable. Two dimensional hexagonal lattice forming a honeycomb structure in the \(xy\)-plane has been periodically repeated along \(z\)-axis with 10 Å spacing to minimize interlayer interactions. In order to reduce the effects of the constraints to be imposed by using the primitive unit cell we performed structure optimizations on the (2x2) cell in the \(xy\)-plane. Our calculations revealed that the planar structure (where all atoms lie in the same plane) is metastable, but it is buckled by 0.45 Å relative vertical displacement of alternate atoms on the hexagons. The gain of energy upon buckling is 30 meV/atom. The binding energy is calculated to be 4.9 eV/atom which is 0.6 eV lower than Si diamond structure and the average distance between nearest Si atoms is 2.2 Å. In the rest of the paper this graphene-like structure will be specified as buckled honeycomb structure. As shown in Fig.1 the detailed band structure and total density of states (TDOS) analysis indicate that both buckled and planar system have large band gaps along \(k \parallel G\) and \(MK\) directions, but conduction and valence bands cross the Fermi level at the \(k\)-point of Brillouin zone. The electronic structure of the system does not change significantly as a result of buckling, except some of the bands split due
to the lowering of the rotation symmetry. Using a similar method but different pseudopotentials and exchange correlation potential Takeda et al. have examined planar and buckled honeycomb structures of Si. Our results obtained in four times larger cell hence allowing more variational freedom are in overall agreement with the results in Ref. Moreover, we performed an ab-initio molecular dynamics calculations on 2x2 supercell providing further evidence that buckled honeycomb structure is stable at 500K for 250 time steps.

Next we address whether a graphite like structure of Si (or graphitic Si) can form? Our study distinguished chemisorption and physisorption states in the interlayer interaction, in contrast to only the physisorption state in graphite. The chemisorption state corresponding to a smaller lattice parameter c = 6 Å is energetically more favorable, namely the binding is 5.1 eV which is 0.4 eV smaller than that of the bulk Si. We note, however, that the lattice parameters, binding energies depend on the approximation of exchange-correlation potential. Present GGA calculations yield relatively larger interlayer distance and requires the incorporation of long range Van der Walls (VdW) interaction. Such an analysis related with the binding of graphite showing that the lattice parameter calculated by GGA is improved upon including VdW attraction has been presented elsewhere.

Similar to Si, the honeycomb structures of AlP, GaAs and GaN are found to be also stable, but less energetic relative to the bulk crystal by 0.8, 1.1 and 0.6 eV per basis, respectively. However, the buckling is not favored in order to hinder the formation of dipole layer.

IV. SINGLE WALL SILICON NANOTUBES
A. Energetics and Stability

Having discussed the stability of Si buckled honeycomb structure (Si-HC), now we present our systematic analysis of (n,0) zigzag and (n,n) armchair SWSiNTs for different n values; namely n = 3 – 14 for zigzag and n = 3, 6, 9 for armchair structures. The (3,0) zigzag SWSiNT has clustered upon structure relaxation indicating that it is not stable even at T=0 K. While the structure optimization has resulted in a regular (4,0) and (5,0) tubular structures, the ab-initio MD calculations showed that these nanotubes eventually transform into cluster at higher temperatures as shown in Fig. Significant distortions can be easily noticed in (6,0) and also (7,0) SWSiNTs, but tubular character and hexagonal structures on the surface have remained. The (6,0) zigzag tube, which has a radius of R = 3.8 Å as well as those with larger radii remain stable at temperatures up to 800 K. Barnard et al. also reported the instability of (3,0) SWSiNT in their first-principles study, but they considered (4,0) and (5,0) SWSiNTs as stable structures depending on their geometry optimization performed at T=0 K. Present results set a limit for fabricating small radius SWSiNTs. The first and second nearest neighbor interactions between Si atoms become relevant for the stability of small radius nanotubes and causes clusterings, if R < 3.8 Å. Similar behavior is also obtained for (n,n) armchair SWSiNTs. For example (3,3) SWSiNT is clustered at 800 K in spite of the fact that geometry optimization yields tubular structure at T=0 K. On the other hand, the (6,6) tube having relatively larger radius remained stable at 800 K after 250 time steps. In contrast to (n,n) SWSiNTs which are found unstable for n < 6, the (3,3) SWCNT is known to be stable and experimentally fabricated. The difference in the chemical behavior of C and Si can be traced to the difference in their bonding capabilities. Si tends to utilize all of its three orbital at a time leading, in turn, to sp^3-hybridization in 1D, 2D and 3D structures. This is the explanation why tubular structures of C are more stable than those of Si. Moreover, since the interatomic distance increases significantly in going from C to Si, the π–π overlap decreases accordingly, resulting in much weaker π-bonding for Si tubes in comparison with that for carbon tubes.

After the discussion of stability, we next analyze the energetics, namely the behavior of binding energy (E_b) as a function of the radius (or n) of the tube. E_b per atom is calculated using the expression,

\[ E_b = \{E_F[SWSiNT] - N(E_F[Si])\}/N \]  

in terms of the total energy of the optimized SWSiNT having N Si atoms per unit cell, E_F[SWSiNT], and the
FIG. 2: Structures of (4,0), (8,0) and (6,6) SWSiNTs at T=0 and T=500K after 250 time steps. Tubular structure has remained in (6,6) and (8,0) SWSiNT, but (4,0) structure has clustered.

FIG. 3: The calculated binding energy per atom for (n,0) zigzag and (n,n) armchair SWSiNTs. Dark region indicates that tubular structures are unstable at finite temperature. The calculated strain energies, $E_S$ per atom for (n,0) and (n,n) SWSiNTs are shown by inset.

B. Mechanical Properties

Radial flexibility is a criterion for the stability of tubular structure. SWCNTs are known to be flexible for the deformations in radial directions; they can sustain severe radial deformation transforming the circular cross section into an elliptical one with minor ($b$) and major ($a$) axis. The radial deformation on a bare tube of radius $R$ is specified in terms of the strain associated with the pressing of the tube along the minor axis, $\epsilon_{yy} = (b - R)/R$ and the strain associated with the expansion of the tube along the perpendicular major axis $\epsilon_{xx} = (a - R)/R$. Theoretical and experimental research have shown that radially deformed tubes relax reversibly to original circular cross section whenever the external radial force is lifted. Moreover, radial deformation can modify the electronic structure reversibly, that leads to a tunable band gap engineering.

Our results indicate that SWSiNTs display a behavior different than that of SWCNTs. We performed a systematic analysis of radial strain for (8,0) zigzag and...
(6,6) armchair SWSiNTs. First, these tubes have been deformed by applying $\epsilon_{yy}=-0.1,-0.2$ and -0.3. Then the stress (or constraint) imposing these radial strains has been lifted and the structure has been optimized. Contrary to situation in carbon nanotubes, up to the applied strain $\epsilon_{yy} \leq -0.2$ the SWSiNTs have remained in deformed state. For example, (8,0) tubes with initial radial strain of $\epsilon_{yy}=-0.1$ and -0.2 are relaxed to a plastic deformation corresponding to $\epsilon_{yy}=-0.09$ and $\epsilon_{yy}=-0.14$, respectively. Similar results have been obtained for (6,6) armchair SWSINT with initial radial strain of $\epsilon_{yy}=-0.1$ and -0.2. In contrast, the tubes, which initially strained by $\epsilon_{yy}=-0.25$ and -0.3 have relaxed to a state with negligible residual strain. The total energy of the undeformed SWSiNT $E_T^n$ have been found to be lower (more energetic) than the total energy $E_T^o(\epsilon_{yy})$ of tubes which were relaxed upon radial deformation $-0.3 \leq \epsilon_{yy} \leq 0$. However, the energy difference $\Delta E = E_T^o(\epsilon_{yy}) - E_T^n > 0$ is very small. The weakness of $\pi$-bonds of Si as compared to carbon nanotubes is possibly a reason why the restoring forces are not strong enough to derive the deformed state to relax back to the original undeformed state. Since the applied radial deformation gets significant ($|\epsilon_{yy}| > 0.2$) the restoring forces become strong enough to derive the relaxation towards circular cross section. On the other hand, after a severe radial strain that causes to a significant coupling between opposite internal surfaces the deformed state may be more energetic (i.e $E_T^o(\epsilon_{yy}) < E_T^n$) or it may relax to different structures such as clusters. This situation constitutes an important difference between Si and C single-wall nanotubes.

Axial strength of SWSiNT, or the elastic stiffness along tube axis is defined as the second derivative of the strain energy per atom with respect to the axial strain $\epsilon_{zz}$, namely $\kappa = d^2E_T/d\epsilon_{zz}^2$. The elastic stiffness of the (8,0) SWSiNT along its axis is calculated to be 23 eV. This value is significant, but smaller than that of SWCNT which is calculated to be 52-60 eV.[57]

C. Electronic Structure

A systematic analysis of electronic structure indicates that metallic zigzag SWSiNTs $6 \leq n \leq 11$ have three bands crossing the Fermi energy, but a band gap between valence and conduction bands opens when $n \geq 12$. Similar effect has been obtained for zigzag SWCNTs when $n \geq 7$. This metal-semiconductor transition was attributed to the energy shift of the singlet $\pi^*$-band which is normally empty, but becomes filled due to increased $\sigma^* - \pi^*$ hybridization at small radius. In the present case it appears that $\sigma^* - \pi^*$ hybridization becomes significant at relatively larger radius. The conductance of all these infinite, perfect tubes ($6 \leq n \leq 11$) is predicted to be equal to $3G_o$ ($G_o = 2e^2/h$). Similar metallic behavior is also obtained for armchair types namely for (6,6) and (9,9) SWSiNTs. The conductance of ideal infinite $(n,n)$ tubes is $2G_o$, but not $3G_o$ as in metallic $(n,0)$ zigzag tubes. Fig. 4 presents the systematic analysis of $(n,n)$ tubes for $7 \leq n \leq 14$ and clearly shows how the singlet $\pi^*$-band gradually raises as $n$ increases.

Based on LDA calculation Fagan et al. also found (6,6) and (6,0) SWSiNT’s metallic, but they predicted (10,0) and (12,0) zigzag nanotubes are semiconductor with a small band gap of 0.1 eV. The disagreement between the present one and those of Fagan et al. may be due to the differences in pseudopotentials and in the approximation of exchange correlation potential. Note that the transition of $(n,0)$ SWSiNTs from metallic to semiconducting state through gap opening may occur at $n$ that is smaller than predicted by the present study as well by Fagan et al., if self-energy correction are taken into account by GW method. Electronic structure analysis performed for the tubes under strain both radially and axially showed that metallic character is not altered but only the position of Fermi level slightly changed due to deformation. The modification of electronic structure with chirality may offer the possibility of fabrication of nanodevices using SWSiNT junctions. On the other hand, SWSiNTs can be used as metallic interconnects, since their conductance is not severely affected by deformation.

D. Interaction of SWSiNT with Atoms and Molecules

The interaction of Si nanotubes with oxygen atom and oxygen molecule is extremely important for technological applications. The adsorption of oxygen atom is studied by placing it initially above a Si-Si bond parallel to
V. STABILIZATION OF SILICON NANOTUBES BY TRANSITION METAL ATOM DOPING

Recently, Singh et al. showed that Si-clusters and Si-tubular structures formed by top-to-top stacking of Si-hexagons can be stabilized by the implementation of TM atoms inside these structures. Those structures are not only stabilized, but also acquired magnetic properties. Earlier, TM atoms are shown to form rather strong bonds with the carbon atoms on the surface of SWCNTs.

Motivated by the work of Singh et al.\[15\], we investigated whether (3,0) SWSiNT can be stabilized in the same manner. The (3,0) tube has radius \( R \sim 2.4\) Å in which interaction between the atoms located at the opposite walls of the tube as well as excess strain on the Si-Si bonds are the prime causes of structural instability even at \( T=0 \) K. On the other hand, the radius of (3,0) is comparable with the sum of ionic radii of V and Si, i.e. \( R_V + R_{Si} = 2.27\) Å, and hence V atoms can easily be accommodated inside the tube. We considered a (3,0) SWSiNT, which has V atoms implemented inside and periodically arranged along the tube axis. Because of supercell geometry used in the calculations both chains of V atoms (V-LC) and (3,0) tube have common lattice parameter (See Fig.\[5\]). The optimized structure, that consists of planar hexagons are stacked with V-LC passing through their centers, has been found to be stable. The energy of the V-stabilized structures is lowered by 12.9 eV relative to the energies of the V-LC and Si-tube without V-LC in it but having the same atomic structures as Si tube with V-LC. Spin-relaxed calculations resulted in zero magnetic moment \( \mu = 0 \). The \( p-d \) hybridization between Si and V atomic orbitals is the cause of stability and lowering the total energy.

The radius of the unrelaxed (3,3) SWSiNT of 3.7 Å is too large and may not be suitable for its stabilization through the implementation of an atomic chain. Perhaps, it may be better suited to accommodate a small clusters of atoms. We considered the possibility whether the (3,3) SWSiNT is stabilized by TM atoms adsorbed on the external surface of the tube. To this end, we studied Ti and Cr atoms adsorbed on the hollow sites.
FIG. 6: Perspective and top (cross section) view of the fully relaxed V-doped (3,0), Ti and Cr doped (3,3) SWSiNTs. Our results revealed that small radius SWSiNTs can be stabilized by doping transition metal element. 

(i.e above the hexagons formed by Si atoms). As shown in Fig. 6 we examined 3 different (3,3)+TM structures; namely 3 Ti-LC, 3 Cr-LC and 6 Cr-LC are adsorbed on the (3,3) SWSiNT surface. Spin-relaxed GGA calculation are carried out to optimize the geometric structure. The external absorption 3 Ti-LC (or 3 Ti atom per unit cell of (3,3) tube) prevented the tube from collapsing into a cluster, but the circular cross section changed to a polygonal one. The ground state has been predicted to be non-magnetic with $\mu = 0$. The external adsorption of 3 Cr-LC also resulted in polygonal cross section, but ferromagnetic ground state with net magnetic moment $\mu = 9.7\mu_B$ (Bohr magneton). The circular cross section is maintained by the adsorption of 6 Cr-LC. This latter structure has also ferromagnetic ground state with $\mu = 17.2\mu_B$.

Calculated energy band structure of (3,0)+V, (3,3)+Ti, (3,3)+3Cr and (3,3)+6Cr are presented in Fig. 7. The (3,0)+V structure is a metal. Six bands crossing the Fermi level yields quantum ballistic conductance of $G=6G_0$. The partial density of states indicates that V-3$d$ and Si-3$p$ orbital character dominate the states at the Fermi level. The (3,3)+3Ti structure is a semiconductor with a very narrow band gap. In the case of (3,3)+3Cr and (3,3)+6Cr several majority (spin-up $\uparrow$) and minority (spin-down $\downarrow$) bands are crossing the Fermi level. Hence both structures are metals with finite density of majority $D(E = E_F, \uparrow)$ and minority $D(E = E_F, \downarrow)$ spin states at $E_F$. However, $D(E = E_F, \uparrow) - D(E = E_F, \downarrow)$ is significant. These properties, which are also dependent on the decoration of the tubes, can be used in nanospintronics device applications. Much recently Dumitrica et al.\[10\] have investigated the stabilization (3,0) zigzag and (2,2) armchair SWSiNTs by various atoms (Zr, Sc, Ti, Cr, Fe, Ni, Be, And Co) axially placed inside the tube. However, they consider neither the magnetic ground state due to specific TM atoms, nor the stabilization of tubes having relatively larger radius.

VI. OTHER TUBULAR STRUCTURES OF SILICON

We now consider different tubular structures which are formed by stacking of atomic polygons as presented in Fig. 8. Three tubular structures given in the first row, i.e. $T_1, T_2, T_3$ are made of triangles of silicon atoms, which are stacked along the axis of the tube. In $T_1$, triangles are identical and placed in top-to-top (or eclipsed) position; in $T_2$ the triangles are staggered; $T_3$ structure is constructed by insertion of a Si-LC into the $T_1$ structure as such that the chain atoms are centered in between the layers. The same convention is followed in labelling the tubular silicon nanowires with pentagonal ($P_1, P_2, P_3$) and hexagonal ($H_1, H_2, H_3$) cross-sections.

Starting with those geometries, structural optimizations in large supercells yielded $T_2, T_3$, and $H_3$ as unstably
FIG. 8: Some tubular structures of Si. The tubes are formed by stacking of Si polygons; the labels T, P, and H stand for triangular, pentagonal, and hexagonal configurations, respectively. $T_1, P_1,$ and $H_1$ tubes have top-to-top arrangement of layers. In $T_2, P_2,$ and $H_2$ the layers are staggered. $T_3, P_3,$ and $H_3$ structures have extra atoms centered in between the layers.

FIG. 9: Energy band structure of Si tubular structures formed by top-to-top stacking of triangular ($T_1$), pentagonal ($P_1$), and hexagonal ($H_1$) polygons. In the right panels the corresponding equilibrium conductance in $G_0 = 2e^2/h$ curves are plotted. The Fermi levels are set to zero.

TABLE I: Structural and conductance properties of silicon tubular structures that are found stable. $E_b$ is the binding energy per atom, $c$ is the unit cell length of the periodic structure, $d$ is the in-plane bond lengths of the polygonal atomic layers. Equilibrium conductance values are given by $G$ in units of conductance quantum, $G_0 = 2e^2/h$.

| Structure | $E_b$ (eV) | $c$ (Å) | $d$ (Å) | $G$ ($2e^2/h$) |
|-----------|-----------|--------|--------|--------------|
| $T_1$     | 4.62      | 2.37   | 2.38   | 6            |
| $T_2$     | –         | –      | –      | –            |
| $T_3$     | –         | –      | –      | –            |
| $P_1$     | 4.79      | 2.37   | 2.37   | 10           |
| $P_2$     | 4.68      | 2.70   | 2.46   | 10           |
| $P_3$     | 4.66      | 4.10   | 2.58   | 6            |
| $H_1$     | 4.77      | 2.29   | 2.37   | 6            |
| $H_2$     | 4.74      | 2.52   | 2.42   | 9            |
| $H_3$     | –         | –      | –      | –            |

Earlier, the pentagonal nanowires of Si and also those of several metals such as Na, Al, Cu, Pb, Au, Fe, Ni, and Xe were investigated by Sen et al. using similar calculation methods. The results for a specific structure, $P_3$, which is common in both studies, is in agreement. The stability of the $P_3$ is further strengthened by the finite-temperature *ab-initio* molecular dynamics calculation carried out in the present study. Recently, Bai et al. have studied the stability of infinite and finite S1 (top-to-top square), $P_1$ and $H_1$ structures by performing *ab-initio* calculations using different methods including pseudopotential plane-waves and classical molecular dynamics calculations at 2000K. Their stability analysis for $P_1$ and $H_1$ are in agreement with present results. In addition to $P_1$ and $H_1$, the present study deals with $T_1$ and also staggered ones.
VII. SINGLE WALL NANOTUBES OF III-V COMPOUNDS

Motivated by interesting properties of SW(BN)NT and opto-electronic and field emitting properties of GaN and AlN tubular forms [21, 25] we choose (8,0) AlP, GaAs and GaN single-wall nanotubes as prototype to investigate the stability and electronic properties of III-V compound nanotubes. Even if the single-wall nanotubes of these compounds have not been synthesised yet, the predictions of present work is essential for further efforts to achieve it. The initial bond lengths are chosen as the distance between nearest cation and anion atoms in bulk structure. After relaxation of all atomic positions, as well as lattice constant \( c \), the tubular structures remained stable. The \textit{ab-initio} MD calculations also showed that SW(AlP)NT remained stable at room temperature after 250 time steps. \( E_b \) is calculated to be 9.6 eV per AlP basis. The radius of the tube is 5.2 \( \AA \). The structure is not a perfect tube but the hexagons on the surface are buckled. The nearest Al-P distance is 2.3\( \AA \), and second nearest neighbor distance \( i.e.\), nearest P-P and Al-Al distances are 3.9\( \AA \) and 3.8\( \AA \), respectively. The energy band and TDOS analysis in Fig. 10 points out that (8,0) SW(AlP)NT is a semiconductor (insulator) with a band gap of 2.0 eV.

Initial tubular structure of (8,0) SW(GaAs)NT is maintained after geometry optimization at \( T=0 \) K. Similar to SW(AlP)NT, hexagons are buckled. \( E_b \) is calculated to be 7.7 eV per GaAs and the radius is 4.8 \( \AA \). The nearest Ga-As distance is 2.4\( \AA \), and nearest Ga-Ga and As-As distances are 3.9\( \AA \) and 4.1\( \AA \), respectively. The (8,0) SW(GaAs)NT is also a semiconductor (insulator) with a band gap of 0.9 eV.

We place a special emphasis on GaN nanotubes [20, 61] which are successfully synthesized by an epitaxial casting method where ZnO nanowires are initially used as templates. GaN nanotubes produced this way have diameter of 300 \( \AA \) and minimum wall thickness of 50 \( \AA \). They are semiconducting and hence they would be a possible candidate for optoelectronic applications. Whether single-wall GaN tube of smaller diameter (2\( R \sim 10 \AA \)) can be stable and can exhibit technologically interesting electronic properties is important to know. We again took (8,0) SW(GaN)NT as prototype for the sake of consistency. Stable tubular geometry is obtained by both geometry optimization at \( T=0 \) K and \textit{ab-initio} MD analysis at \( T=800 \) K. Upon relaxation atoms on the surface are buckled. \( E_b \) is calculated to be 11.5 eV per GaN and the radius is 4.1 \( \AA \). The nearest Ga-N distance is 1.8\( \AA \), and nearest Ga-Ga and N-N distances are 3.1\( \AA \) and 3.2\( \AA \), respectively. We found that the (8,0) SW(GaN)NT is a semiconductor (insulator) with a band gap of 2.2 eV. Previous first-principles study performed by Lee et al. [22] by using LDA method predicted the similar band gap for SW(GaN)NT. Here, we examine also whether SW(GaN)NT is radially elastic. To this end we started with the elliptically deformed nanotube under \( \epsilon_{yy} = -0.1 \), and let it relax in the absence of radial forces. Similar to the Si nanotube, SW(GaN)NT is found to be radially soft.

For the sake of comparison, the binding energy and bond distance of bulk crystal, honeycomb structure, and (8,0) tubular structures of Si, AlP, GaN, and GaAs are presented in Table II. In these structures the covalent or (covalent-ionic) mixed bonds have different orbital combinations. While bulk crystals are tetrahedrally coordinated and have bonds formed by \textit{sp}^3-hybrid orbitals, in honeycomb and tubular structures bonding through \textit{sp}^2-hybrid orbitals dominates the cohesion.
TABLE II: Calculated binding energies $E_b$ and bond distances $d$ in Å of various structures of Si, AlP, GaAs, and GaN. B:3D bulk crystal, H:2D honeycomb structure, T: (8,0) single wall nanotube structure. The units of binding energy is eV/atom for Si, and eV/atom for III-V compounds.

|       | Si       | AlP     | GaN     | GaAs    |
|-------|----------|---------|---------|---------|
| $E_b$ (eV) | 5.4 4.9 4.8 | 10.4 9.6 9.6 | 12.4 11.8 11.5 | 8.3 7.2 7.7 |
| $d$ (Å)  | 2.3 2.3 2.3 | 2.4 2.2 2.3 | 2.0 1.8 1.8 | 2.4 2.2 2.4 |

VIII. CONCLUSION

In this paper, we analyzed the stability of Si and III-V compound, single-wall nanotubes and calculated their optimized atomic structure and energy band structure. Si as well as III-V compounds can form stable 2D honeycomb structure, which is precursor of nanotubes. The energy necessary to roll these honeycomb structures over a cylinder of radius $R$ to make a perfect nanotube is however small as compared to those in carbon nanotubes. We found that Si single-wall nanotubes with small radius are unstable and are clustered either at $T=0$ K or at finite temperatures. For example, while (3,0) is unstable even at $T=0$ K, (4,0) and (5,0) lose their tubular character and tend to form cluster at $T=500$ K. Stable (n,0) zigzag SWSiNTs are metallic for $6 \leq n \leq 11$, but become semiconducting for $n \leq 12$. The metallicity of small radius $(n,0)$ tubes is a typical curvature effect and is resulted from the dipping of the singlet $\pi^*$-band into the valence band at small radius. Stable $(n,n)$ armchair SWSiNTs $(n=6,9)$ are metallic. Our study on radially deformed $(8,0)$ and $(6,6)$ SWSiNTs demonstrated that these nanotubes are radially "soft", and hence are devoid of strong restoring force that maintains radial elasticity. The radial softness of Si tubes is a behavior which distinguishes them from carbon nanotubes. In contrast to that axial stiffness the Si nanotube has ben found to be high. We predicted that oxygen molecule adsorbed on the Si-Si bonds dissociates. A strong interaction between O/O$_2$ and SWSiNT appears to be serious in future processes involving Si tubes. Adatoms like Si, Au and H can also form strong chemisorption bonds with the atoms on the surface of SWNT. We showed that unstable, small radius SWSiNTs can be stabilized through the implementation or external adsorption of 3d transition metal atoms. In particular, the decoration of the tube surface by the external adsorption of transition metal atoms can lead magnetic properties which may find potential technological applications. Small radius tubular structures different than those based on honeycomb structure have been identified. Finally, we found III-V compound $(8,0)$ nanotubes (AlP, GaAs, and GaN) stable at least at room temperature and they are semiconductor with band gap ranging from 0.9 eV to 2.2 eV. In contrast to small radius metallic Si nanotubes, $(8,0)$ compound nanotubes are semiconductor. The band gap increases with decreasing row number of elements. Even though not all the structures treated in this study have not been realized experimentally yet, the predictions obtained from the present first-principles calculations are expected to be essential for further research in this field.

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