PHYSICAL REVIEW B **78**, 165425 (2008)

First-principles study of silicon nitride nanotubes

Guohua Gao[*] and Hong Seok Kang[†]
Department of Nano and Advanced Materials, College of Engineering, Jeonju University, Hyoja-dong,
Wansan-ku, Chonju, Chonbuk 560-759, Republic of Korea

(Received 17 July 2008; revised manuscript received 19 September 2008; published 27 October 2008)

We have made a first-principles calculation of the topological, geometric, and electronic structures of nitrogen-doped armchair and zigzag silicon carbide nanotubes, where we have assumed that all carbon atoms have been substituted by nitrogen atoms. The doping was found to be substantially easier than for analogous carbon nanotubes. In addition, the doping process is cooperative, leading us to theoretically predict the stable existence of silicon nitride nanotubes (SiNNTs). For (n,n) SiNNTs, all kinds of chiral indices n are possible. These armchair tubes are semiconductors with much smaller band gaps than those of corresponding silicon carbide nanotubes, and the gap decreases with the tube diameter. For $(n,0)$ chirality, only even-numbered chiral indices $(n=2l)$ are possible. These nanotubes are also semiconductors with band gaps larger than those of armchair SiNNTs of similar diameters.

DOI: 10.1103/PhysRevB.78.165425 PACS number(s): 61.48.De, 61.46.Fg

I. INTRODUCTION

Carbon nanotubes (CNTs) are an interesting quasi-one-dimensional system with diverse electronic properties that depend on the chirality of the structures.[1] However, this very fact limits their application in nanoelectronic devices because, in practice, it is very difficult to separate semiconducting tubes from metallic ones by a simple procedure. Therefore, nanoelectronic applications would benefit from other kinds of nanotubes that have unique electronic properties that do not depend on chirality. This kind of nanotube might be found by substituting carbon atoms with a pair of heteroatoms. The first known example is that of boron nitride nanotubes (BNNTs),[2] which were synthesized after theoretical prediction.[3] They are insulators with a large band gap independent of chirality.

Very recently, silicon carbide nanotubes (SiCNTs) were synthesized from the reaction of SiO and multiwalled CNTs[4] and one half of the carbon atoms in the CNTs were substituted by silicon atoms. In SiCNTs, carbon and silicon atoms exist in a 1:1 ratio, and a theoretical calculation shows that the tubes consist of alternating C and Si atoms forming sp^2 Si-C bonds.[5] Single-walled SiCNTs are known to be semiconductors regardless of their chirality.

Heteroatom doping is a convenient way to modulate the chemical, mechanical, and electronic properties of nanotubes. For example, nitrogen doping of CNTs can convert them to *n*-type materials. Since Miyamoto *et al.*[6] predicted that graphitic C_3N_4 and CN mostly have tubular forms, experimental work to synthesize CN_x nanotubes with controllable composition has attracted much attention.[7] Typical doping concentrations of nitrogen atoms range from 0.05% to 1.02%. In an effort to achieve a similar doping of SiCNTs, it will be valuable to investigate the possible synthesis of $SiCN_x$ nanotubes, produced through substitutional doping of SiCNTs in which some carbon atoms are replaced by nitrogen atoms. The extreme case of such doping would result in silicon nitride nanotubes (SiNNTs), where all the carbon atoms of the tubes are substituted by nitrogen atoms, producing Si and N atoms in a 1:1 ratio. The present work will investigate the topology, mechanism, and energetics of the doping process that results in SiNNTs from a first-principles calculation. In addition, we will also investigate the geometric and electronic structures of SiNNTs.

TABLE I. Energy changes in eV of doping per nitrogen atom $[=\Delta E(2)/2]$ of the process SiCNT+2N $\rightarrow$2N-SiCNT+2C for various isomers of SiCNTs in comparison with the corresponding values for CNTs.

		$\Delta E(2)/2$			
		SiCNT			CNT
Chirality	d (Å)[a]	Z	A	R	R
(5,5)	8.44	1.58	1.65	2.18	3.28
(6,6)	10.28	1.64	1.69	2.26	3.29
		Z	E	R	R
(8,0)	7.98	1.51	1.54	1.69	3.11
(10,0)	10.10	1.59	1.65	2.03	3.34

[a] The diameter of the tube.

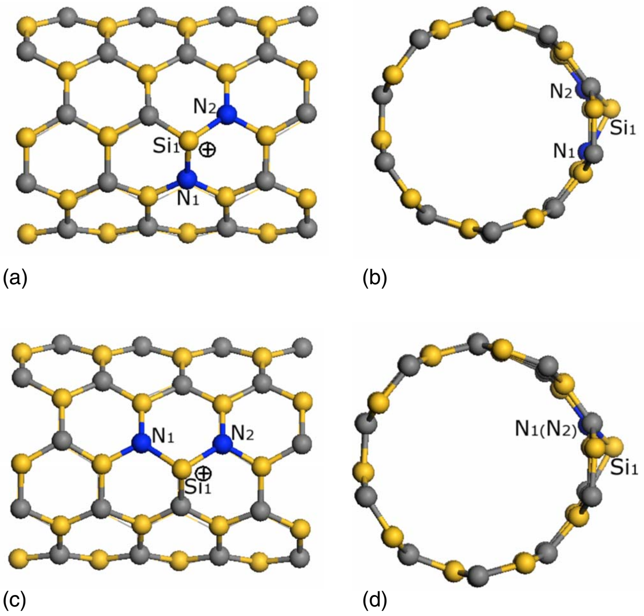

FIG. 1. (Color online) Two different views for isomers of (5,5) 2N-SiCNT: [(a) and (b)] isomers Z and [(c) and (d)] A. The plus sign indicates that the corresponding atom protrudes from the circumference of the tube.

II. THEORETICAL METHODS

Total energy calculations were performed using the Vienna *ab initio* simulation package (VASP).[8] Electron-ion interactions were described by the projected augmented wave (PAW) method.[9] Exchange-correlation effects were treated within the local-density approximation (LDA). The cut-off energy was set high enough (=400 eV) to ensure accurate results, and the conjugate gradient method was employed to optimize the geometry until the Hellmann-Feynman force exerted on each atom was less than 0.03 eV/Å.

In order to investigate the effect of chirality and diameter on the doping, we took supercells which consisted of four primitive cells of (5,5), (6,6), and (8,8) SiCNTs, and we considered three primitive cells of (8,0), (10,0), and (12,0) tubes. The total number of atoms in the four primitive cells of armchair tubes were 80, 96, and 128, respectively. The corresponding values in the three primitive cells of zigzag tubes were 96, 120, and 144, respectively. The lattice parameters were 12.24 and 15.96 Å for supercells of (n,n) and $(n,0)$ SiCNTs, respectively.

In each tube, two or four carbon atoms were substituted by nitrogen atoms. In order to do this, four k points were used for k-point sampling in the irreducible region of the first Brillouin zone of the supercell along the tube axis $(=X)$. We also investigated the limiting case in which all carbon atoms were substituted by nitrogen atoms, for which we adopted a supercell which consisted of one primitive cell of SiNNT. We used large supercells that guaranteed that interatomic distances between neighboring cells along the Y and Z directions were greater than 10 Å.

III. RESULTS

First, we investigate nitrogen substitution of SiCNTs. The energy change of doping per atom $\Delta E(n_N)/n_N$ is defined as the energy change of the doping process, SiCNT$+n_N$N $\rightarrow$2N-SiCNT$+n_N$C $(n_N=2)$, divided by the number of nitrogen atoms $(=n_N)$. Table I shows this energy change for various isomers in comparison with that of the corresponding processes for CNTs. (Chemical potentials of N and C atoms adopted are for atomic states.) Surprisingly, the results show that the N doping of SiCNTs is drastically easier than that of CNTs regardless of the chirality of the tube. This result can be ascribed to the fact that Si-N bonds are more polar than Si-C bonds because N atoms are more electronegative than C atoms.[10]

We now concentrate on describing our results for the doping on four primitive cells of a (5,5) tube. Figure 1 shows two isomers of 2N-SiCNT, Z and A, where the first isomer is slightly more stable (see Table I). In both isomers, two nitrogen atoms are located at "adjacent" sites in such a way that there is a sequence of N_1-Si_1-N_2 bonds. In isomer A, the line joining N_1 and N_2 is parallel to the tube axis, which is not the case in isomer Z. Si_1 protrudes from the circumference of the doped tubes by 0.65–0.80 Å. According to Table I, the possibility of doping at random sites $(=R)$ in which two N atoms are not adjacent to each other can be excluded, since this is much less favorable ($\sim$0.6 eV). [Note that this is in contrast to the case of N doping of CNTs, where the random doping (R) or the formation of two rows of pyridinelike local structures along the tube axis (P) is the most favorable.[11]]

Table II shows that there are many isomers which are comparable to one another in energy when two more nitrogen atoms are doped, where isomer AAa is the most stable. By our convention, the two uppercase letters indicate two kinds of motives for 2N doping. Figure 2 shows that each

TABLE II. Energy change in eV of doping per nitrogen atom $[=\Delta E(4)/4]$ of the process SiCNT+4N $\rightarrow$4N-SiCNT+4C for various isomers of armchair SiCNTs in comparison with the corresponding values for CNTs.

	SiCNT							CNT	
Chirality	AAa	AZa	ZZa	AAs	AZs	ZZs	R	P[a]	R
(5,5)	1.49	1.54	1.56	1.57	1.61	1.64	2.09	3.34	3.39
(6,6)	1.54	1.55	1.61	1.69	1.66	1.64	2.17	3.53	3.42

[a] The isomer in which two pairs of nitrogen atoms form two rows along the tube axis in such a way that a $(4n+2)\pi$ local system with four pyridinelike structures is formed. See Ref. 11 for more details.

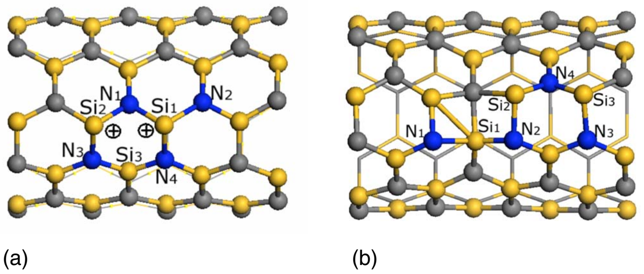

FIG. 2. (Color online) Two most stable isomers of (5,5) 4N-SiCNT: isomers (a) AAa and (b) AZa. The plus sign indicates that the corresponding atom protrudes from the circumference of the tube.

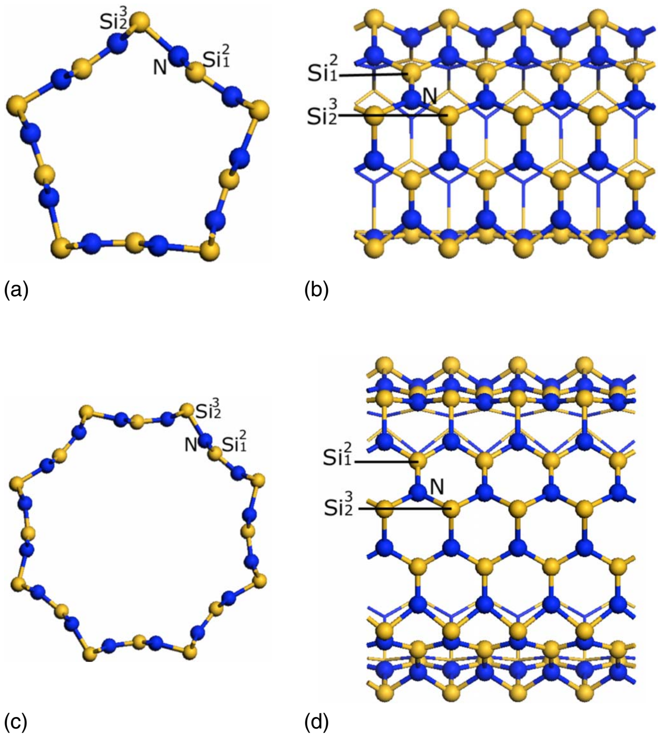

FIG. 3. (Color online) Two different views for armchair SiNNTs: [(a) and (b)] (5,5) and [(c) and (d)] (8,8) tubes. For a better understanding, four primitive cells are shown.

pair of nitrogen atoms forms isomer A of a 2N-SiCNT in such a way that the two pairs are located adjacent to each other. (The lowercase letters "a" and "s" represent that the two motives are adjacent to and far from each other, respectively.)

The table shows two important results valid for both (5,5) and (6,6) tubes. First, a careful comparison of the results shows that the doping is more favorable in smaller diameter tubes, which seems to correlate with the fact that silicon atoms can adopt sp^3-hybridization more easily in smaller diameter tubes. Second, the N doping that results in the most stable isomer is cooperative; that is, the doping of two more N atoms is easier once two N atoms are doped beforehand. In fact, Table III shows that the cooperativity is even more pronounced in the limiting case in which all the carbon atoms are substituted by nitrogen atoms to form SiNNTs, as evidenced by the values of $\Delta E(n_{\mathrm{N}})/n_{\mathrm{N}}$. (For this calculation, we used 15 k points in the irreducible region of the first Brillouin zone of the primitive cell.) They are smaller than the values of $\Delta E(4)/4$ for 4N-SiCNTs shown in Table II. Once N doping is initiated in SiCNTs, particularly in tubes of small diameters, it can easily propagate to the adjacent sites, eventually leading to the formation of SiNNTs. A comparison of $\Delta E(n)/n$ of the (12,12) tube in Table III with $\Delta E(2)/2$ of the (6,6) tube in Table I and $\Delta E(4)/4$ of the (6,6) tube in Table II shows that the cooperativity in N doping still exists for large tubes with diameters of ~2 nm. This is because $\Delta E(2)/2$ and $\Delta E(4)/4$ of the (12,12) tube will be larger than those of the (6,6) tube.

Figure 3 shows that the geometric structures of (n,n)

TABLE III. Energetic and electronic parameters of SiNNTs. Values in parentheses correspond to values for the respective SiCNTs.

L_x [a]	Chirality	$\Delta E(n_{\mathrm{N}})/n_{\mathrm{N}}$ (eV)	E_{gap} (eV)[b]	Location[c]	ΔE_{roll} (eV)[d]	d (Å)[e]	
2.85	(5,5)	1.29	0.49(2.20)	Indirect(indirect)	−1.28(0.16)	7.64(8.44)	8.42(8.44)
2.85	(6,6)	1.34	0.50(2.19)	X(indirect)	−1.27(0.11)	9.77(10.28)	11.01(10.28)
2.85	(8,8)	1.41	0.31(2.32)	X(indirect)	−1.26(0.06)	12.62(13.51)	14.16(13.51)
2.85	(12,12)	1.47	0.10(2.42)	X(indirect)	−1.23(0.03)	19.03(20.37)	20.52(20.37)
4.95	(8,0)	1.26	1.14(1.32)	Indirect(Γ)	−1.28(0.19)	8.09(7.98)	8.93(7.98)
4.95	(10,0)	1.28	1.08(1.73)	Indirect(Γ)	−1.33(0.12)	9.33(9.88)	10.16(9.88)
4.95	(12,0)	1.30	1.07(1.88)	Indirect(Γ)	−1.34(0.08)	11.52(11.80)	12.39(11.80)
4.95	(20,0)	1.36	1.02(2.26)	Indirect(Γ)	−1.34(0.03)	18.47(19.48)	19.26(19.48)

[a] The lattice parameter of a primitive cell along the tube axis.

[b] The band gap of the SiNNT.

[c] The location of the band gap when it is direct.

[d] Energy change per pair of Si-N (Si-C) atoms upon rolling up the SiN (SiC) sheet into the corresponding tube.

[e] Diameters of inner and outer shells of armchair tubes. For zigzag tubes, they correspond to the innermost and the outermost shells.

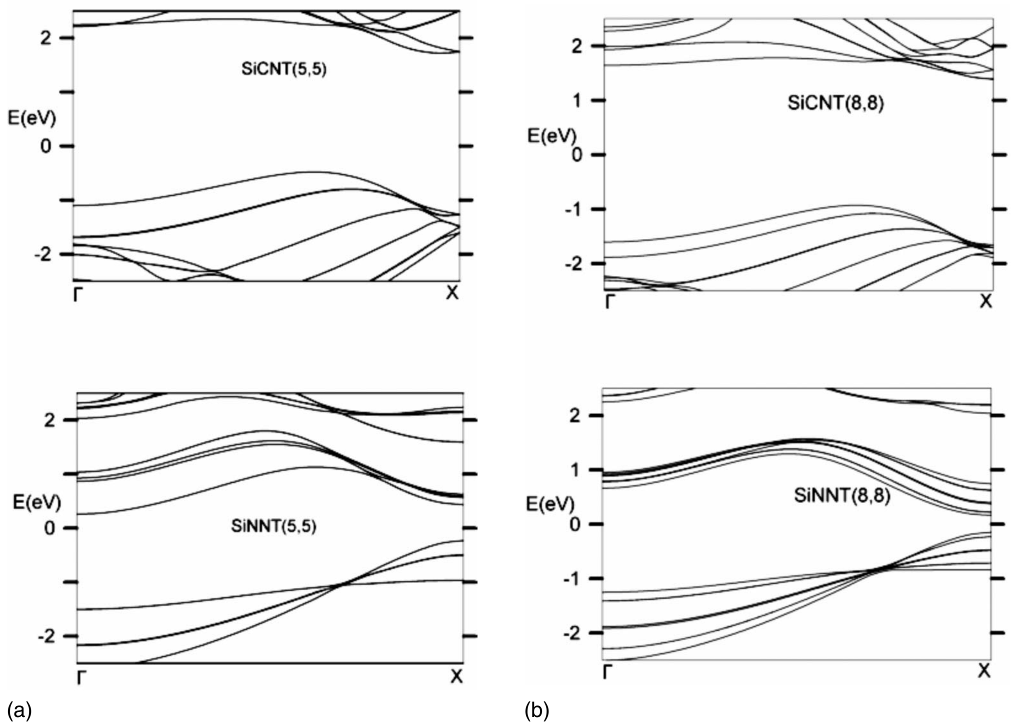

FIG. 4. Band structures of armchair SiNNTs in comparison with those of SiCNT: (a) (5,5) and (b) (8,8) tubes.

SiNNTs exhibit star-shaped rotational (=C_n) symmetry along the tube axis. All Si atoms (=Si_1^2) on the inner layer are sp^2-hybridized, as evidenced by the near planarity of the local geometry around them. Here, a layer is defined as a set of atoms in the same X position along the tube axis. In contrast, all Si atoms (=Si_2^3) on the outer layer, which are nearly sp^3-hybridized, occupy the apices of the underlying polyhedron, as viewed along the tube axis, since they protrude from the circumference of the tube. In fact, two of three N-Si-N angles (~94°) spanned by the atoms deviate significantly from 120° for the sp^2 hybridization. Meanwhile, all nitrogen atoms are sp^2 hybridized. As a result, the lattice constant of a primitive cell of armchair SiNNTs (=2.85 Å) is smaller than that of the corresponding SiCNT (=3.06 Å).

Figure 4 compares the band structures of primitive cells of pristine (5,5) and (8,8) SiNNTs with those of corresponding SiCNTs. In general, we expect a gradual increase in the effect of *n*-type doping as the degree of N doping becomes higher. In fact, our analysis shows that the energy difference between donor states and the bottom of the conduction band gradually decreases with the number of nitrogen atoms, eventually resulting in a band gap of 0.49 eV in the extreme case of the (5,5) SiNNT. In fact, Table III shows that the gap is indirect and substantially smaller than that of the corresponding SiCNT (=2.20 eV). For the (5,5) tube, the conduction-band minimum is located at Γ point, and the value of $E_n(k)$ at point X is slightly higher than that at the Γ point. For (6,6) and larger tubes, the minimum is located at point X, resulting in direct band gaps. Furthermore, the gap also decreases with the tube diameter, and the gap is very small for the (12,12) SiNNT (=0.10 eV). This observation is related to the fact that the valence band and the conduction band are characterized by pronounced π-electron densities at the Si_2^3 and Si_1^2 atoms, respectively, noting that the two kinds of Si atoms become equivalent in the limit of an infinite diameter.

Next, we describe our investigation on the N doping of three primitive cells of zigzag SiCNTs. Table I compares values of $\Delta E(2)/2$ for doping with two nitrogen atoms in zigzag tubes. As Fig. 5 shows, there are two stable isomers, Z and E, in which two Si atoms are adjacent in such a way that there is also a sequence of N-Si-N bonds. Similar to the

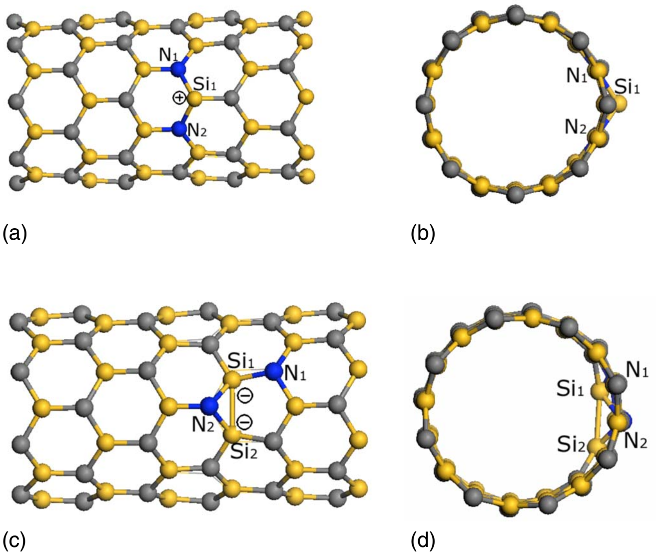

FIG. 5. (Color online) Two different views for isomers of (8,0) 2N-SiCNT: isomers [(a) and (b)] E and [(c) and (d)] Z. The plus or minus sign indicates that the corresponding atom either protrudes from the circumference of the tube or sinks into the tube.

TABLE IV. Energy change in eV of doping per nitrogen atom $[=\Delta E(4)/4]$ of the process SiCNT+4N $\rightarrow$4N-SiCNT+4C for various isomers of zigzag SiCNTs in comparison with the corresponding values for CNTs.

Chirality	SiCNT							CNT
Isomer	EZa	ZZa	EEa	EZs	ZZs	EEs	R	R[a]
(8,0)	1.42	1.47	1.50	1.56	1.60	1.54	1.80	3.18
(10,0)	1.51	1.55	1.59	1.61	1.57	1.65	2.04	3.34

[a] Corresponding values for isomer P of CNTs are not shown, since the isomer is much less stable than isomer R for zigzag CNTs. See Ref. 11 for more details.

case of armchair tubes, the isomers are distinguished from each other by the relative positions of the two N atoms. The line joining the two N atoms is perpendicular to the tube axis in isomer E, which is not the case in isomer Z. As in the case of armchair tubes, these configurations are more stable than isomer R in which two N atoms are randomly positioned.

Here, we will describe the case when four nitrogen atoms are doped in zigzag tubes. Table IV shows that isomer EZa is the most stable, followed by isomer ZZa (see Fig. 6 for their structures). Comparing the values of $\Delta E(4)/4$ for those isomers [=1.42 and 1.47 eV for (8,0) tube] with that of random doping (=1.80 eV) again indicates the tendency of the pairs to be adjacent to each other. Comparing the values of $\Delta E(2)/2$, $\Delta E(4)/4$, and $\Delta E(n)/n$ in Tables I, IV, and III also shows that the doping is increasingly cooperative as more nitrogen atoms are doped.

Table III shows various parameters for zigzag SiNNTs where all carbon atoms are substituted by Si atoms. For this calculation, we used 11 k points in the irreducible region of the first Brillouin zone of the primitive cell. Figure 7 shows that the geometrical structures of the $(n,0)$ SiNNTs exhibit $C_{n/2}$ rotational symmetry along the tube axis. This observation indicates that only $(2l,0)$ chiralites will be observed for zigzag tubes, where l is an integer. These isomers also have pronounced quadruple-shell structures, in which the outermost shells have diameters that are 9%–10% larger than the innermost ones (see Table III). The figure shows that the atoms in each shell are N_1, Si_2, N_3, and Si_4, respectively. All Si_2 atoms are almost sp^2-hybridized, as evidenced by the near planarity of the local geometry around the atom. On the other hand, one half of the Si_4 atoms ($=Si_4^3$), which are nearly sp^3-hybridized, occupy the apices of the underlying polyhedron viewed along the tube axis, protruding from the circumference of the tube. In fact, all three N-Si_4^3-N angles ($\sim$97°) of the atoms deviate significantly from 120° for sp^2-hybridization. The other half of the Si_4 atoms ($=Si_4^2$) are almost sp^2-hybridized. In summary, only one fourth of Si atoms of the tube are sp^3-hybridized, while one half adopts the same hybridization as in armchair tubes. Our consideration of the hybridization of N atoms leads us to conclude that the total number of sp^3-hybridized atoms is conserved irrespective of the chirality of the SiNNT. Namely, we find that one half of N_1 atoms, i.e., one fourth of all N atoms of $(n,0)$ SiNNTs are sp^3-hybridized. Therefore, one fourth of all atoms of the tube are sp^3-hybridized, since one fourth of all Si atoms are also sp^3-hybridized as already explained. As a result, the lattice constant of a primitive cell of a zigzag SiNNT (=4.95 Å) is smaller than that of the corresponding SiCNT (=5.32 Å).

Figure 8 shows the band structure of (8,0) and (12,0) SiNNTs in comparison with those of corresponding SiCNTs. The valence-band maximum is located at the Γ point, causing the gap to be indirect, and the value of $E_n(k)$ at point X is slightly lower for all zigzag tubes investigated in this work. As is also shown in Table III, the band gap also decreases with the tube diameter. In the valence band, the electron density is largely concentrated on Si_4^3 atoms, while it is

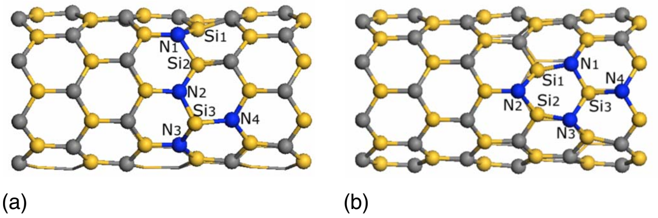

FIG. 6. (Color online) Two most stable isomers of (8,0) 4N-SiCNT: isomers (a) EZa and (b) ZZa.

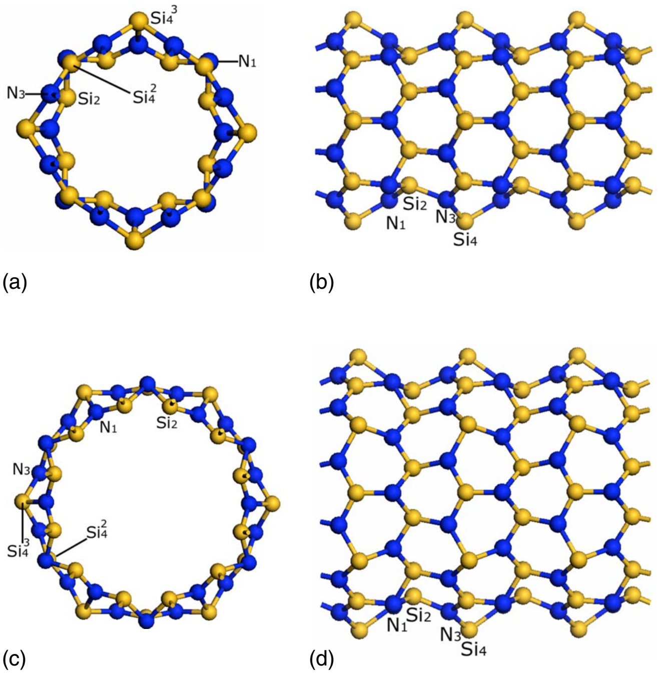

FIG. 7. (Color online) Two different views for zigzag SiNNTs: [(a) and (b)] (8,0) and [(c) and (d)] (12,0) tubes.

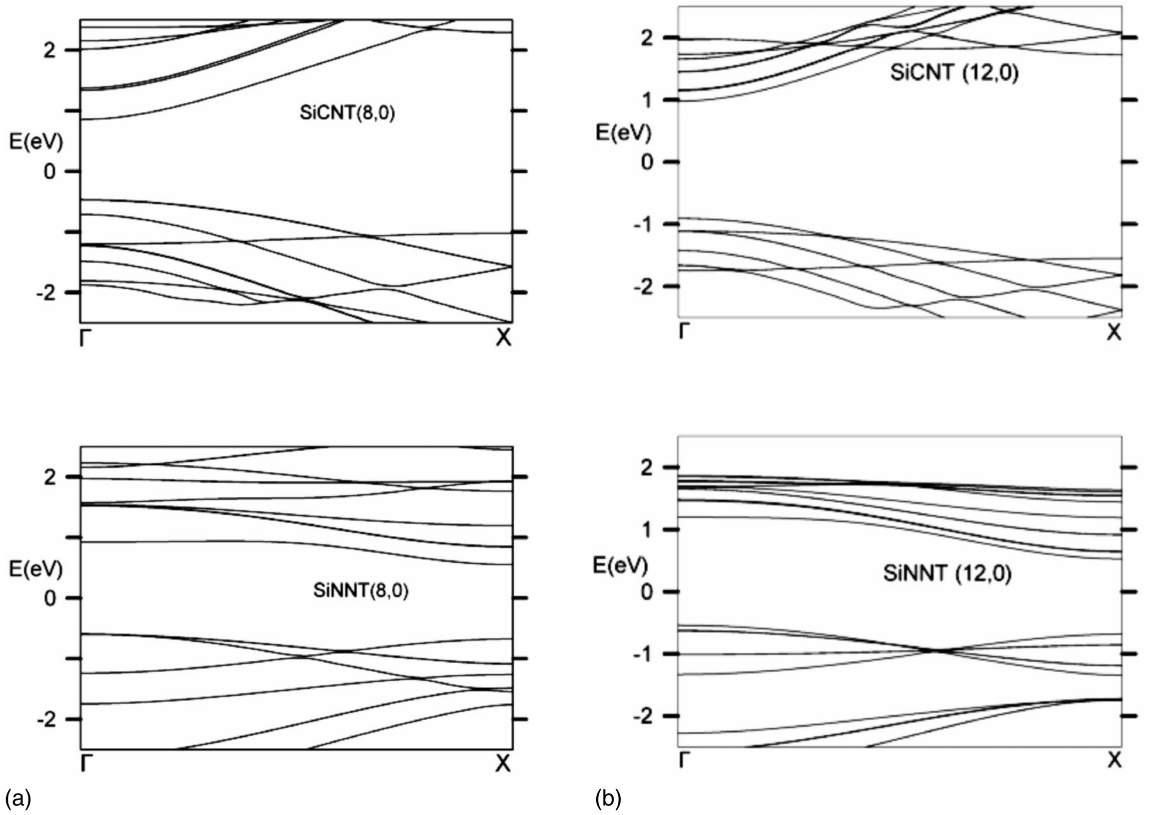

FIG. 8. Band structures of zigzag SiNNTs in comparison with those of SiCNT: (a) (8,0) and (b) (12,0) tubes.

concentrated on the Si_4^2 atoms in the conduction band. The gap is significantly larger than that of an armchair tube of a similar diameter, which is even the case for (20,0) tube for which the gap has almost reached its asymptotic value. This observation can be understood if we note that the (8,0) tube is relatively square when viewed along the tube axis, while the (5,5) tube is relatively pentagonal. Namely, the hybridization natures of Si_4^2 and Si_4^3 are more different from each other in the zigzag tubes than the corresponding atoms in the armchair tubes of similar diameters.

It will be also of interest to investigate the relative stability of SiNNTs in comparison with those of SiN sheet and SiCNTs. Optimal lattice constants for the rhombus of the two-dimensional primitive cell is found to be 3.07 and 3.02 Å for SiC and SiN sheets, respectively, when we assume that the sheets have $P3m1$ symmetry. Table III shows the values of energy of rolling ($=\Delta E_{\mathrm{roll}}$), which corresponds to the energy change per pair of atoms upon rolling up the sheet into the corresponding tube. As expected, SiNNTs are more stable than SiN sheets in which all Si atoms adopt sp^2 hybridization, while the opposite is true for SiCNTs. For armchair SiNNTs, tubes of larger diameters are less stable than those of smaller diameters. This is because Si_2^3 atoms can adopt sp^3 hybridization less easily in larger tubes. On the other hand, zigzag SiNNTs are more stable when the diameters are larger, and it seems that the quadruple-shell structure discussed above is responsible for this stabilization. Indeed, Table III shows that the (20,0) SiNNT is appreciably more stable than the (12,12) SiNNT, even though they have similar diameters. Therefore, zigzag tubes will dominate over armchair tubes in SiNNTs of large diameters.

IV. CONCLUSION

From first principles, we have investigated the topological, geometric, and electronic structures of the nitrogen-doped armchair and zigzag SiCNTs, where carbon atoms are replaced by nitrogen atoms. First, the doping is substantially easier than that for corresponding CNTs. In addition, the initial doping occurs at adjacent sites and propagates to proximal sites. Furthermore, the doping process is cooperative in that it is easier as more nitrogen atoms are doped. These observations lead us to theoretically justify the existence of SiNNTs in which all carbon atoms are substituted by nitrogen atoms, resulting in 1:1 ratio of Si and N atoms. In fact, our calculation has shown that SiNNTs of diameters of at least 2 nm can be generated by N doping. We also find that zigzag tubes will dominate over armchair tubes in SiNNTs of diameters larger than 2 nm.

For (n,n) SiNNTs, all kinds of chiral indices n are possible. The tubes exhibit C_n rotational symmetry along the tube axis, where one half of the nitrogen atoms occupy apices with sp^3 hybridization. The tubes are semiconductors with band gaps much smaller than those of corresponding SiCNTs, and the gap decreases with the tube diameter. In fact, the gap is very small (=0.10 eV) for (12,12) SiNNT. For $(n,0)$ chirality, only even-numbered chiral indices ($n=2l$) are possible. These tubes show $C_{n/2}$ rotational symmetry along the tube axis, where one fourth of the nitrogen atoms occupy apices. They are also semiconductors with band gaps smaller than those of corresponding SiCNTs, but larger than those of armchair SiNNTs of similar diameters, which can be understood in terms of the band-structure analysis. Although the band gaps are underestimated by the LDA, we expect that the analysis of the electronic structures described in this work will be qualitatively correct. It is also interesting to note the semiconducting properties of SiNNTs, considering that similar carbon nitride nanotubes with a 1:1 atomic ratio are expected to show metallic behaviors.[6]

Finally, it is worth mentioning that the N doping can introduce defects and vacancies, which can lead to the distortion of the tubular structures or the formation of bamboolike structures. However, the possibility should be smaller than that for CNTs because of a strong tendency of N atoms to bind with Si atoms.

ACKNOWLEDGMENTS

We appreciate Jeonju University for financial support. We also acknowledge support from KISTI under the 11th Strategic Supercomputing Applications Support Program.

---

[*] Also at Pohl Institute of Solid State Physics, Tongji University, Shanghai 200092, People's Republic of China.

[†] Corresponding author. hsk@jj.ac.kr

[1] P. J. F. Harris, *Carbon Nanotubes and Related Structures* (Cambridge University Press, Cambridge, 1999).

[2] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, Science **269**, 966 (1995).

[3] A. Rubio, J. L. Corkill, and M. L. Cohen, Phys. Rev. B **49**, 5081 (1994); X. Blasé, A. Rubio, S. G. Louie, and M. L. Cohen, Europhys. Lett. **28**, 335 (1994).

[4] X. H. Sun, C. P. Li, W. K. Wong, N. B. Wong, C. S. Lee, S. T. Lee, and B. K. Teo, J. Am. Chem. Soc. **124**, 14464 (2002).

[5] M. Menon, E. Richter, A. Mavrandonakis, G. Froudakis, and A. N. Andriotis, Phys. Rev. B **69**, 115322 (2004); Y. Miyamoto and B. D. Yu, Appl. Phys. Lett. **80**, 586 (2002); A. Mavrandonakis, G. E. Froudakis, M. Schnell, and M. Muhlhauser, Nano Lett. **3**, 1481 (2003).

[6] Y. Miyamoto, M. L. Cohen, and S. G. Louie, Solid State Commun. **102**, 605 (1997).

[7] X. Wang, Y. Liu, D. Zhu, L. Zhang, H. Ma, N. Yao, and B. Zhang, J. Phys. Chem. B **106**, 2186 (2002); C. Cao, F. Huang, C. Cao, J. Li, and H. Zhu, Chem. Mater. **16**, 5213 (2004); L. H. Chan, K. H. Hong, D. Q. Xiao, T. C. Lin, S. H. Lai, W. J. Hsieh, and H. C. Shih, Phys. Rev. B **70**, 125408 (2004); Y. Xiong, Z. Li, Q. Gou, and Y. Xie, Inorg. Chem. **44**, 6506 (2005).

[8] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); G. Kresse and D. Joubert, *ibid.* **59**, 1758 (1999).

[9] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).

[10] A Si-N bond will have a larger binding energy than a Si-C bond in the sp^2 network of the tube since the former bond is more polar. A similar phenomenon is observed for the binding energy of a Si-X single bond in molecules when X changes from C to F. See J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry*, 4th ed. (Harper Collins, New York, 1993), p. A-32.

[11] H. S. Kang and S. Jeong, Phys. Rev. B **70**, 233411 (2004).