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ORIGINAL PAPER

NMR parameters of SiC-doped (6,0) *zigzag* single-walled boron phosphide nanotubes: a density functional study

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Abstract Nuclear magnetic resonance (NMR) parameters including isotropic and anisotropic chemical shielding parameters and electronic structures were calculated using density functional theory (DFT) for silicon–carbide-doped boron phosphide nanotubes. Geometry optimizations were carried out at the B3LYP/6-31G* level of theory using the Gaussian 03 program suite. The isotropic and anisotropic chemical shielding parameters were calculated for the sites of various ^{13}C, ^{29}Si, ^{11}B, and also ^{31}P atoms in pristine and SiC-doped (6,0) *zigzag* boron phosphide nanotube models. The calculations indicated that doping of ^{11}B and ^{31}P atoms by C and Si atoms had a more significant influence on the calculated shielding tensors than did doping of the B and P atoms by Si and C atoms. In comparison with the pristine model, Si- and C-doping of P and B sites of the *zigzag* nanotubes reduces the energy gaps of the nanotubes and increases their electrical conductance.

Keywords Boron phosphide nanotubes · Silicon carbide · Chemical shielding · DFT

Introduction

Since the synthesis of carbon nanotubes (CNTs) [1], single-walled carbon nanotubes (SWCNTs) have attracted great interest owing to their physical and chemical properties [1–3] and applications as novel materials [4, 5]. The electronic properties of CNTs depend on their tubular diameter and chirality. Many investigations have been undertaken to investigate non-carbon-based nanotubes, which exhibit electronic properties independent of these features. Among these, boron nitride nanotubes (BNNTs) and boron phosphide nanotubes (BPNTs), which are made from the group III and V elements neighboring C in the Periodic Table, are an interesting subject of many studies [6–10]. BNNTs are inorganic proportions of carbon nanotubes (CNTs) and have good physical properties for a broad variety of applications [11]. BNNTs are semiconductors with almost the same band gap of 5.5 eV [12], and they are chemically and thermally stable [13–16]. Because of the slight positive charge of B and slight negative charge of N, the polarity and ionicity of the nanotubes are increased. Therefore, BNNTs are considered as more appropriate materials than CNTs for applications in specific electronic and mechanical devices. However, the properties of BNNTs have been studied more often than those of BPNTs [17, 18], and further study of the electronic properties of BPNTs remains interesting.

Nuclear magnetic resonance (NMR) spectroscopy is one of the best techniques to study the electronic structure properties of matter [19]. Moreover, doping of

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BPNTs by Si and C atoms may be able to yield changes in the interactions between the nanotube and foreign atoms or molecules. Therefore, the objective of the present work is to study the properties of the electronic structure of SiC-doped BPNTs by performing density functional theory (DFT) calculations of NMR parameters of representative (6,0) *zigzag* BPNT models (Fig. 1). The electronic structure properties, including bond lengths, energies, band gaps, and NMR parameters in both pristine and the SiC-doped BPNT structures, are investigated by calculations of the chemical shielding (CS) tensors at the sites of various ^{13}C, ^{29}Si, ^{11}B, and ^{31}P atoms.

Results and discussion

Structures of the BPNTs

The structural properties consisting of the B–P bond lengths, energies, and band gaps for the investigated models of the (6,0) *zigzag* BPNTs are summarized in Table 1. There are two forms of triple SiC-doped BPNT for the (6,0) *zigzag* model, where the B and P atoms are doped by Si and C atoms (Fig. 1a, Si_BC_p) or the B and P atoms are doped by C and Si atoms (Fig. 1b, Si_PC_B). There are B–P, B–C, Si–P, and Si–C bonds in Fig. 1a (Si_BC_p) and there are B–P, B–Si, C–P, and Si–C bonds in Fig. 1b (Si_PC_B).

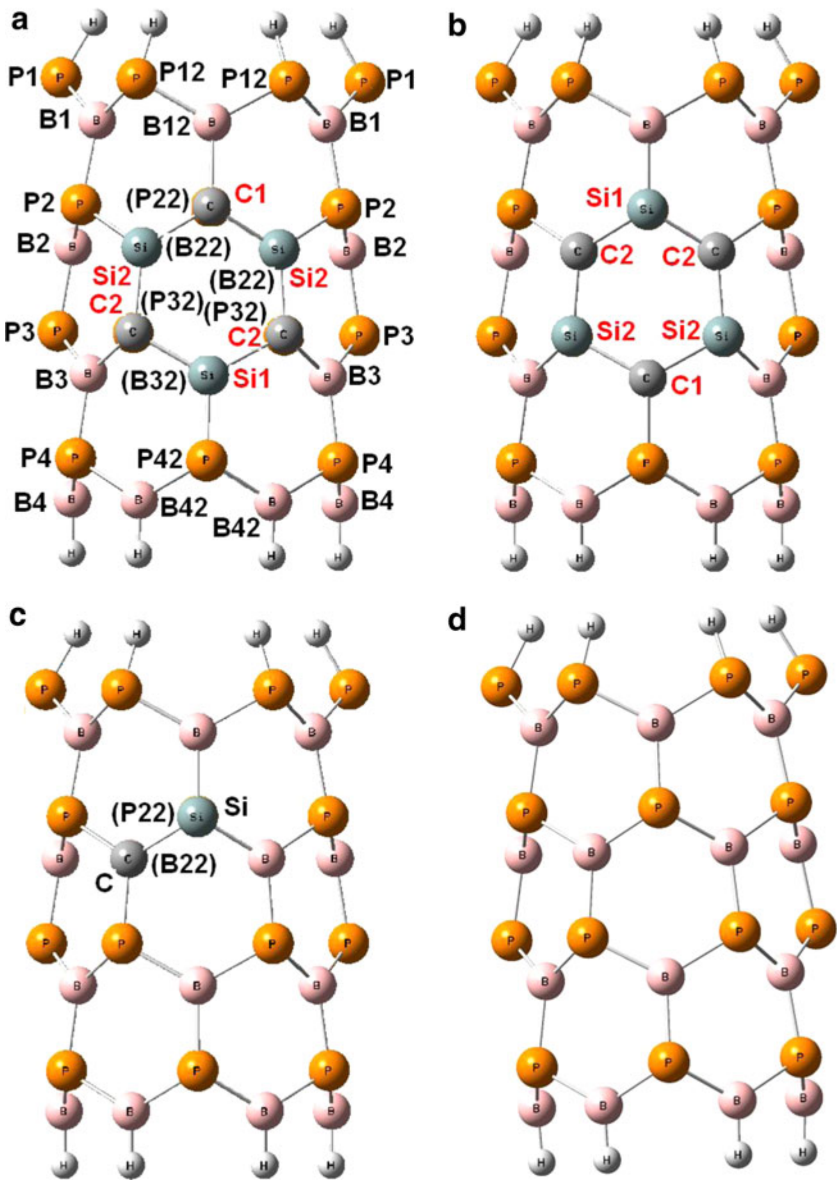

Fig. 1 **a**, **b** Two-dimensional (2D) views of triple Si_BC_P and Si_PC_B doped (6,0) *zigzag* BPNTs; **c** 2D views of single Si_PC_B doped (6,0) *zigzag* BPNTs; **d** 2D views of pristine (6,0) *zigzag* BPNTs

Table 1 Structural properties of representative (6,0) *zigzag* BPNT models

Property	Fig. 1a	Fig. 1b	Fig. 1c	Fig. 1d
Bond length (Å)				
B1-P1	1.904	1.918	1.942	1.904
B2-P2	1.936	1.933	1.933	1.903
B3-P3	1.972	1.889	1.904	1.902
B4-P4	1.885	1.889	1.889	1.885
B12-P12	1.944	1.872	1.871	1.904
B22-P22	–	–	–	1.903
B32-P32	–	–	1.898	1.902
B42-P42	1.904	1.872	1.878	1.885
B12-P22	–	–	–	1.894
B22-P32	–	–	1.854	1.891
B32-P42	–	–	1.905	1.898
B12-C1	1.527	–	–	–
B12-Si1	–	1.986	–	
Si2-C1	1.793	1.808	–	–
Si2-C2	1.786	1.786	–	–
Si1-C2	1.788	1.787	–	–
Si1-P42	2.198	–	–	–
C1-P42	–	1.799	–	–
Si–C	–	–	1.788	–
Si–B	–	–	1.971	–
C-P32	–	–	1.801	–
Energy (keV)	−236.218	−236.215	−238.319	−239.372
Band gap (eV)	2.38	1.83	1.86	2.27

The calculated results showed that the B–P bond lengths are almost the same in the investigated models of the (6,0) *zigzag* BPNTs. In Fig. 1a, the value of the Si1-P42 bond length is the largest whereas that of B12-C1 is the shortest among the different types of bonds in the investigated models. The Si–C bond lengths are almost the same in the investigated models of the (6,0) *zigzag* BPNTs. Also, the calculated energies and the values are the same for the two forms (a and b) of SiC-doped BPNTs. However, the band gaps showed differences between the two forms (Fig. 1a, b). In comparison with the pristine model, the band gap of Fig. 1a is closer to the pristine model, whereas Fig. 1b is significantly reduced in the (6,0) *zigzag* BPNTs and increases their electrical conductance. These results show that the doping of B and P atoms by C and Si atoms (Fig. 1b, $\mathrm{Si_PC_B}$) has more influence on the band gap of the BPNTs than does doping of the B and P atoms by Si and C atoms (Fig. 1a, $\mathrm{Si_BC_P}$).

NMR parameters of the (6,0) zigzag BPNTs

The NMR parameters for the investigated models of the (6,0) *zigzag* BPNTs are summarized in Table 2. In the pristine model of the (6,0) *zigzag* BPNTs, the NMR parameters are separated into four layers (Table 2; Fig. 1d), which means that the CS parameters for the atoms of each layer have equivalent chemical environment and electrostatic properties. In Fig. 1a ($\mathrm{Si_BC_p}$), the B22 and B32 atoms are doped by Si atoms and P22 and P32 are doped by C atoms, which results in B–C, Si–P, and Si–C bonds. The calculated results in Table 2 show that the NMR parameters of the various B atoms in Fig. 1a ($\mathrm{Si_BC_p}$) of the SiC-doped *zigzag* BPNTs show some significant changes due to the SiC-doping, except for the B12 and B3 atoms. Among the B atoms of Fig. 1a ($\mathrm{Si_BC_p}$), B12 and B3 are directly bonded to C atoms; hence, both the $\mathrm{CS^I}$ and $\mathrm{CS^A}$ parameters show important changes due to the SiC-doping. However, both the $\mathrm{CS^I}$ and $\mathrm{CS^A}$ parameters for B1, B2, and B42 atoms show some changes due to an indirect effect of the B atoms on the Si atom, and atom B4 does not exhibit any significant changes due to the SiC-doping in the (6,0) *zigzag* BPNTs. Among the P atoms of Fig. 1a ($\mathrm{Si_BC_p}$), in comparison with the pristine model, the greatest changes in the NMR parameters are observed for the P2 and P42 atoms, and both the $\mathrm{CS^I}$ and $\mathrm{CS^A}$ parameters show significant changes because of the contribution to the chemical bonding with the Si atoms. Except for the change in the $\mathrm{CS^I}$ and $\mathrm{CS^A}$ parameters for the P12 atom, the changes in the $\mathrm{CS^I}$ and $\mathrm{CS^A}$ parameters are not very important for the other P atoms, which are indirectly bonded to the SiC-doped (6,0) *zigzag* BPNTs in Fig. 1a ($\mathrm{Si_BC_p}$).

In Fig. 1b ($\mathrm{Si_PC_B}$), the P22 and P32 atoms are doped by Si atoms and the B22 and B32 atoms are doped by C atoms on the (6,0) *zigzag* BPNTs, which yields B–Si, C–P, and Si–C bonds. Among the B atoms, the most important changes in both NMR parameters ($\mathrm{CS^I}$ and $\mathrm{CS^A}$) are observed for the B12 atom, which is directly bonded to the Si atoms. The $\mathrm{CS^I}$ parameters of the B3 and B4 atoms do not exhibit any significant changes due to the SiC-doping in the (6,0) *zigzag* BPNTs (Fig. 1b), but the $\mathrm{CS^A}$ parameters of atom B3, which is directly bonded to the Si atoms, exhibit significant changes, whereas the $\mathrm{CS^A}$ parameters of the B4 atom show some significant changes. Also, both the $\mathrm{CS^I}$ and $\mathrm{CS^A}$ parameters for B1, B2, and B42 atoms show some changes due to the indirect effect of the B atoms on the C atoms. In Fig. 1b ($\mathrm{Si_PC_B}$), the P2 and P42 atoms are directly bonded to C atoms. The most significant changes in both NMR parameters ($\mathrm{CS^I}$ and $\mathrm{CS^A}$) of the P atoms of Fig. 1b ($\mathrm{Si_PC_B}$), in comparison with the pristine model of the (6,0) *zigzag* BPNTs, are observed for the P42 atom. The most significant changes in the $\mathrm{CS^A}$ parameters are observed for the P2 atom, which is directly bonded to the C atoms. The changes in the values of the CS parameters for the P1 and P12 atoms, which are indirectly bonded to the SiC-doped ring, are also notable. The $\mathrm{CS^A}$ parameters of

Table 2 NMR parameters (ppm) of representative models of the (6,0) *zigzag* BPNTs

Nucleus	Fig. 1a		Fig. 1b		Fig. 1c		Fig. 1d	
	CS^I	CS^A	CS^I	CS^A	CS^I	CS^A	CS^I	CS^A
B1	12.13	148.95	21.18	142.50	15.97	144.06	17.9	143.8
B12	38.31	114.15	32.52	154.86	29.32	161.21	17.9	143.8
B2	26.64	122.35	26.48	112.63	32.18	107.04	30.7	115.9
B22	–	–	–	–	–	–	30.7	115.9
B3	39.82	87.96	25.44	135.18	23.35	117.08	25.1	117.5
B32	–	–	–	–	35.97	112.31	25.1	117.5
B4	39.09	127.96	39.77	122.23	39.77	125.63	39.7	126.5
B42	34.65	131.62	46.99	121.18	40.04	126.38	39.7	126.5
P1	375.16	110.70	392.88	87.40	402.45	93.94	383.1	114.9
P12	396.38	131.98	359.75	158.32	344.12	145.74	383.1	114.9
P2	459.64	175.89	385.53	159.81	383.83	140.88	373.9	249.9
P22	–	–	–	–	–	–	373.9	249.9
P3	348.66	251.34	342.36	250.87	360.40	243.75	341.6	247.6
P32	–	–	–	–	285.58	220.01	341.6	247.6
P4	333.05	271.60	331.34	300.31	340.13	264.19	333.7	274.3
P42	407.11	202.73	268.89	245.22	327.43	279.51	333.7	274.3
C1	81.86	167.66	65.99	180.02	37.48	190.56	–	–
C2	74.96	136.65	83.45	148.07	–	–	–	–
Si1	213.49	251.60	254.75	188.22	252.51	246.69	–	–
Si2	229.10	162.01	274.53	191.49	–	–	–	–

the P3 and P4 atoms exhibit significant changes due to the indirect effect of the P atoms on the Si atoms, whereas their CS^I parameters remained almost unchanged. In summary, in Fig. 1b (Si_PC_B), the CS^A and CS^I parameters of all of the P atoms (except for P3 and P4) exhibit significant changes due to direct and indirect effects of the P atoms on the SiC-doped ring.

The values of the NMR parameters (CS^I and CS^A) of the ^{13}C and ^{29}Si atoms in the SiC-doped (6,0) *zigzag* BPNTs are summarized in Table 2. The results in Table 2 show that the values of the CS^I and CS^A parameters of the ^{13}C and ^{29}Si atoms in Fig. 1b (Si_PC_B) are larger than those in Fig. 1a (Si_BC_p) in the (6,0) *zigzag* BPNTs except that the CS^I parameter of atom C1 and the CS^A parameter of atom Si1 in Fig. 1a (Si_BC_p) are larger than in Fig. 1b (Si_PC_B). Comparison of the calculated NMR parameters in Figs. 1a and b shows that the properties of the electronic structure of Fig. 1b (Si_PC_B) of the SiC-doped (6,0) *zigzag* BPNTs, where the B atoms are doped by C atoms and the P atoms are doped by Si atoms (Si_PC_B), are more strongly influenced than those of Fig. 1a (Si_BC_p), where the B atoms are doped by Si atoms and the P atoms are doped by C atoms (Si_BC_P). This trend is in agreement with the change in the band gap of Fig. 1b (Si_PC_B) in comparison with the pristine model of the (6,0) *zigzag* BPNTs. The band gaps of Fig. 1a (Si_BC_p) and the pristine model are almost the same, but the band gaps of Fig. 1b (Si_PC_B) are smaller than those of the pristine model (Table 1).

Effect of SiC concentration on BPNT properties

We studied the effect of the doping concentration on the properties of the (6,0) *zigzag* BPNTs. Because significant changes in the properties of the BPNTs were detected for the Si_PC_B form (Fig. 1b), further calculations were performed with single doping of the (6,0) *zigzag* BPNTs by the SiC dopant in the Si_PC_B form (Fig. 1c). In the model, the B and P atoms were doped by C and Si atoms, respectively. Therefore, the concentration of this type of SiC-doping was studied as a representative model of SiC-doped BPNTs. In Fig. 1c, one BP part has been doped by one SiC part in the (6,0) *zigzag* BPNTs. In comparison with the triple SiC-doped BPNTs (Fig. 1b, Si_PC_B), the results in Table 1 show that the single SiC-doped BPNTs (Fig. 1c) show no significant changes in bond length for the Si–C and B–Si bonds, and the calculated bond lengths are similar to the triple SiC-doped BPNTs (Fig. 1b, Si_PC_B). The Si–C and B–Si bond lengths are 1.788 and 1.971 Å for the single SiC-doped (6,0) *zigzag* BPNTs (Table 1). The calculated band gap of the single SiC-doped (6,0) *zigzag*

BPNT is also very close to that of the triple SiC-doped in Fig. 1b, and the value of the band gap is 1.86 eV, which is smaller than that of the pristine model. Similar results were observed for the NMR parameters of the single and triple SiC-doped BPNTs in which the most significant changes in the values of the B and P nuclei due to the SiC-doping were observed for the atoms nearest to the doping atoms. Comparison of the results for SiC-doped BPNTs using the single and triple SiC-doped models showed that the only significant effects of SiC-doping concentration were reflected by the band gap, which was significantly reduced on increasing the dopant (SiC) concentration.

Conclusions

We studied the NMR parameters including isotropic and anisotropic chemical shielding parameters of silicon–carbide (SiC)-doped boron phosphide nanotubes (BPNTs) by means of DFT calculations. On the basis of our calculations, doping of the B and P atoms by C and Si atoms had more significant influence on the calculated CS tensors than did doping of the B and P atoms by Si and C atoms in the BPNTs. Also, the band gap of Fig. 1a is closer to the pristine model, whereas the band gap of Fig. 1b is significantly reduced with respect to pristine in the (6,0) *zigzag* BPNTs and increases its electrical conductance. The changes in the CS parameters due to the SiC-doping are more significant for the P atoms than for the B atoms with respect to the pristine model. Comparison of the results of the SiC-doped BPNTs for single and triple SiC-doped models showed that the only significant effects of SiC-doping concentration were found in the values of the band gap.

Methods

In the present work, the electronic structure properties of BPNTs were studied by using representative models of (6,0) *zigzag* BPNTs in which the ends of nanotubes were saturated by hydrogen atoms. Each of the representative models has three forms (Fig. 1), namely the pristine model (Fig. 1d) and models where B and P atoms are doped by Si and C atoms, respectively (Si_BC_P, Fig. 1a), or B and P atoms are doped by C and Si atoms, respectively (Si_PC_B, Fig. 1b). We investigated the effect of doping concentration on the properties of the BPNTs. Further calculations were performed with single doping of (6,0) *zigzag* BPNTs by SiC (Fig. 1c). In this model, the B and P atoms were doped by C and Si atoms (Si_PC_B). The hydrogenated models of (6,0) *zigzag* single-walled BPNTs consisted of 60 ($B_{24}P_{24}H_{12}$) atoms. In the first step, the structures were allowed to relax all atomic geometrical parameters in the optimization at the DFT level of B3LYP exchange-functional and 6-31G* standard basis set. Then, the CS tensors were calculated in the optimized structures by using B3LYP/6-31G* for the sites of various ^{13}C, ^{29}Si, ^{11}B, and ^{31}P atoms. It is noted that, in DFT methods, B3LYP is more popular due to its more reliable results in comparison with experiments [20, 21]. Moreover, in a previous study, it has been found that the NMR parameters calculated by B3LYP and B3PW91 levels are in good agreement [20]. The calculated CS tensors in the principal axis system (PAS) with the order $\sigma_{33} > \sigma_{22} > \sigma_{11}$ [22] were converted into measurable NMR parameters [isotropic chemical shielding CS (CS^I) and anisotropic chemical shielding CS (CS^A) parameters] using Eqs. (1) and (2) [23]. All calculations were carried out by using the Gaussian 03 suite of programs [24].

$$CS^{I}(\text{ppm}) = 1/3\,(\sigma_{11} + \sigma_{22} + \sigma_{33}), \tag{1}$$

$$CS^{A}(\text{ppm}) = \sigma_{33} - 1/2(\sigma_{11} + \sigma_{22}). \tag{2}$$

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