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ORIGINAL PAPER

SiC-doped boron nitride nanotubes: computations of ^{11}B and ^{14}N quadrupole coupling constants

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Abstract Density-functional theory calculations have been performed to investigate the properties of the electronic structures of silicon–carbon-doped boron nitride nanotubes (BNNTs). The geometries of zigzag and armchair BNNTs were initially optimized and the quadrupole coupling constants subsequently calculated. The results indicate that doping of B and N atoms by C and Si atoms has more influence on the electronic structure of the BNNTs than does doping of B and N atoms by Si and C atoms. The changes of the electronic sites of the N atoms are also more significant than those of the B atoms.

Keywords Density-functional theory · Electronic structure · Nuclear quadrupole resonance · Nanostructures

Introduction

The discovery of carbon nanotubes (CNTs) by Iijima [1] has motivated intensive studies on the determination and characterization of the properties of this fascinating novel material [2, 3]. Moreover, the stable structures of non-carbon-based nanotubes have also been investigated, among which boron nitride nanotubes (BNNTs) are the most important [4–6]. A growing number of studies have since been devoted to the investigation of structural and electronic properties of BNNTs using experimental [7, 8] and theoretical [9, 10] methods. The stable tubular structure of BNNTs was initially recognized by calculations [11] and subsequently synthesized experimentally [12]. CNTs act as a metal or semiconductor, depending on their tubular diameter and chirality, but BNNTs are viewed as always being semiconductors, independent of the restricting structural factors [13]. The slight negative charge of the nitrogen (N) atom and the slight positive charge of the boron (B) atom increase the polarity of BNNTs, in contrast to CNTs, which are nonpolar. BNNTs have been suggested as potential materials for use in specific applications in electronic and mechanical devices.

Earlier studies investigated the effects of impurities and doping atoms on properties of the electronic structures of BNNTs [14, 15]. To date, doping of BNNTs by Si and C atoms separately has been investigated [16, 17]; however, the counterparts of the Si and C atoms in a doped system have rarely been studied. In this study, the influences of silicon–carbon doping (SiC doping) on the properties of electronic structures of zigzag and armchair BNNTs (Figs. 1, 2) were investigated. To this end, density-functional theory (DFT) calculations were performed to relax the geometries of the investigated structures and calculate the quadrupole coupling constants (C_Q) for ^{11}B and ^{14}N atoms. The C_Q parameter is highly insightful in investigations of electronic and structural properties of this material, and could reveal important trends regarding the electronic sites of B and N atoms in BNNTs [18, 19].

Results and discussion

Figure 1a–c shows two-dimensional views of pristine, Si_NC_B-doped, and Si_BC_N-doped models of the investigated zigzag BNNTs. Figure 1d shows a longer tubular structure of the Si_BC_N-doped model, which was considered to validate the reliability of the calculated parameters regarding

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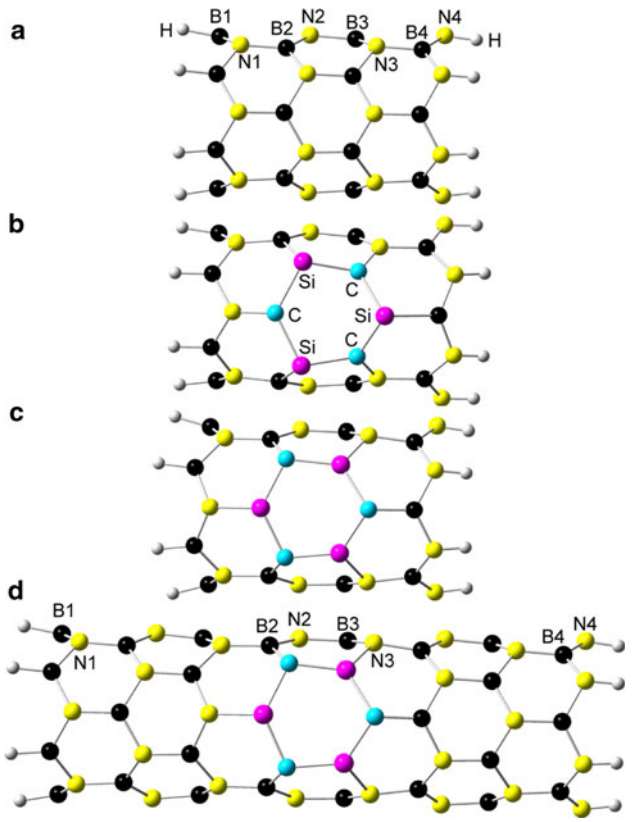

Fig. 1 Models of zigzag BNNTs; model 1: pristine (**a**), model 2: Si_NC_B doped (**b**), model 3: Si_BC_N doped (**c**), model 4: longer tubular form of model 3 to validate the model size in calculations (**d**). For simplicity, two-dimensional (2D) views are shown

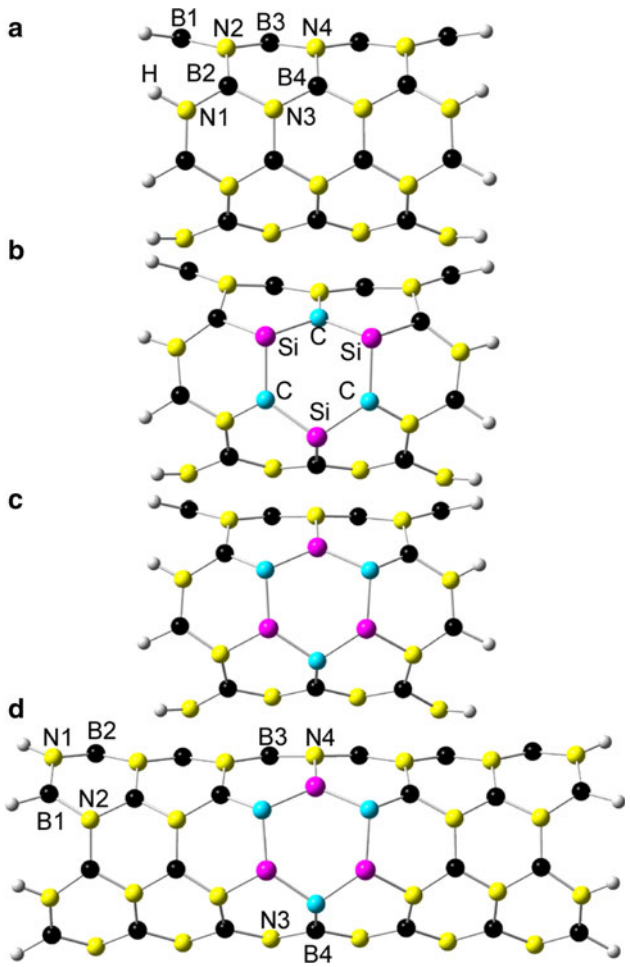

Fig. 2 Models of armchair BNNTs; model 1: pristine (**a**), model 2: Si_NC_B doped (**b**), model 3: Si_BC_N doped (**c**), and model 4: longer tubular form of model 3 to validate the model size in calculations (**d**). For simplicity, two-dimensional (2D) views are shown

the size of the investigated models of the SiC-doped BNNTs. The calculated C_Q parameters for the ^{11}B and ^{14}N atoms of these models are listed in Table 1. B_1–B_4 and N_1–N_4 represent the atomic layers of the BNNT, for which averaged values of six atoms of each layer were calculated. The zigzag BNNTs have two different ends, i.e., B-terminated and N-terminated ones, as indicated in Fig. 1 by B_1 and N_4 layers. The ends of nanotubes are saturated by hydrogen atoms. Comparison of the calculated C_Q parameters of the three zigzag BNNT models indicates that the electronic sites of the B atoms of the B_1 layer exhibit similar changes for the two SiC doping processes. However, the electronic sites of these atoms exhibit differences in the second layer, B_2, where more changes are seen for the Si_NC_B-doped model than for the Si_BC_N-doped model. The changes of the electronic sites of the B atoms of the third layer, B_3, are similar for the two SiC-doped BNNT models. However, the electronic sites of the B atoms of the fourth layer, B_4, of the Si_NC_B-doped model exhibit greater changes than does the Si_BC_N-doped model. In conclusion, the electronic sites of the B atoms in the Si_NC_B-doped BNNT exhibit greater changes than in the Si_BC_N-doped BNNT.

Table 1 Quadrupole coupling constants of the zigzag models

C_Q (MHz)	Model 1 (pristine)	Model 2 (Si_NC_B doped)	Model 3 (Si_BC_N doped)	Model 4 (validation)
B_1	3.52	3.48	3.48	3.53
B_2	2.74	2.84	2.72	2.69
B_3	2.70	2.64	2.62	2.63
B_4	2.53	2.61	2.52	2.53
N_1	0.95	1.08	0.99	0.95
N_2	1.04	0.78	1.02	1.05
N_3	1.14	1.44	1.16	1.11
N_4	2.50	2.45	2.53	2.52

See Fig. 1 for details. The C_Q values for B_1–B_4 and N_1–N_4 are average values for the atoms of each layer. Model 4 is a longer tubular form of model 3 to validate the model size in calculations

The electronic sites of the N atoms of the fourth layer, N_4, which is the N-terminated end of the zigzag BNNT, exhibit different changes in the two SiC-doped BNNTs, as

shown by their C_Q values. The electronic sites of the N atoms of the third layer, N_3, of the Si_NC_B-doped model exhibit significant changes, whereas their changes in the Si_BC_N-doped model are negligible compared with the pristine model. Significant changes are also seen for the N atoms of the second layer, N_2, of the Si_NC_B-doped model, whereas those of the Si_BC_N-doped model remain negligible. The changes of the electronic sites of the N atoms of the first layer, N_1, are notable for the Si_NC_B-doped model, whereas they are negligible for the Si_BC_N-doped model. As a first trend we note that, since the N atom has a lone pair of electrons but the B atom lacks electrons in the valence shell, the changes of the electronic sites of the N atoms are more significant than those of the B atoms on SiC doping. As a second trend, we note that the BNNTs are polar structures because of the different electronegativities of the B and N atoms. It is known that the electronegativity of the N atom is larger than that of the B atom, and the electronegativity of the C atom is larger than that of the Si atom. The polarity of the Si_NC_B-doped model is much more perturbed by the SiC doping than by the Si_BC_N doping. Therefore, compared with the pristine model, the electronic sites of the B and N atoms of the Si_NC_B-doped model exhibit more significant changes than those of the Si_BC_N-doped model. Comparing the results of the two models of the Si_BC_N-doped BNNTs with different tubular lengths (Fig. 1c, d) indicates that the C_Q values of the investigated atomic layers do not reflect the changes of the length of the nanotube in the zigzag models, validating the reliability of the calculated parameters for the SiC-doped BNNTs. The reliability of the tubular sizes investigated in this study was also confirmed in earlier works [14, 15].

Figure 2a–c shows two-dimensional views of pristine, Si_NC_B-doped, and Si_BC_N-doped models of the investigated armchair BNNT. Figure 2d shows the longer tubular structure of the armchair Si_BC_N-doped model, which is considered in order to validate the reliability of the calculated parameters regarding the investigated tubular size of the SiC-doped BNNT. The calculated C_Q parameters for the ^{11}B and ^{14}N atoms of these models are presented in Table 2. B_1–B_4 and N_1–N_4 represent the atomic layers of the BNNT, for which the averaged values of four atoms of each layer are calculated. In contrast to the zigzag BNNTs, the armchair models have two similar ends, consisting of both B and N atoms, as indicated in Fig. 2 by B_1 and N_1 layers. The ends of the nanotube are saturated by hydrogen atoms. Comparison of the calculated C_Q parameters of three models of the armchair BNNT reveals that the electronic sites of the B atoms of the B_1 layer exhibit similar effects for the two SiC doping processes. In the second layer, B_2, the electronic sites of the B atoms of the Si_NC_B-doped model exhibit stronger effects than for the Si_BC_N-doped model. The electronic sites of the B atoms of the third layer, B_3, of both SiC-doped models exhibit similar effects. In the fourth layer, B_4, the electronic sites of the B atoms of the Si_NC_B-doped model exhibit greater changes than for the Si_BC_N model. In agreement with the results for the zigzag BNNTs, the electronic sites of the B atoms in the Si_NC_B-doped model of the armchair BNNT exhibit more changes than for the Si_BC_N-doped model.

Table 2 Quadrupole coupling constants of the armchair models

C_Q (MHz)	Model 1 (pristine)	Model 2 (Si_NC_B doped)	Model 3 (Si_BC_N doped)	Model 4 (validation)
B_1	3.11	3.10	3.08	3.12
B_2	2.67	2.77	2.70	2.67
B_3	2.68	2.62	2.63	2.63
B_4	2.67	2.76	2.63	2.63
N_1	1.84	1.82	1.83	1.84
N_2	0.90	1.21	1.08	0.91
N_3	0.76	0.73	0.77	0.80
N_4	0.86	1.11	0.87	0.84

See Fig. 2 for details. The C_Q values for B_1–B_4 and N_1–N_4 represent averaged values for the atoms of each layer. Model 4 is a longer tubular form of model 3 used to validate the model size in calculations

The electronic sites of the N atoms of the first layer, N_1, exhibit similar effects in the two SiC-doped and also the pristine models of the armchair BNNT, as seen from their C_Q values. The electronic sites of the N atoms of the second layer, N_2, of both SiC-doped models exhibit significant effects, whereas the changes for the Si_NC_B-doped model are more significant compared with the pristine model. The effects of SiC doping on the electronic sites of the N atoms of the third layer, N_3, of both SiC-doped models are similar to those in the pristine model. However, the changes of the electronic sites of the N atoms of the fourth layer, N_4, are significant for the Si_NC_B-doped model but negligible for the Si_BC_N-doped model. As a first trend, we note that the changes of the electronic sites of the N atoms are more significant than for the B atoms on SiC doping of the armchair BNNT. As a second trend, we note that, since the polarity of the Si_NC_B-doped model is much more perturbed by the SiC doping than by the Si_BC_N doping, the electronic sites of the B and N atoms of the former model exhibit more significant changes than the latter, compared with the pristine model. Comparison of the results of the two models of the armchair Si_BC_N-doped BNNT with different tubular lengths (Fig. 2c, d) also indicates that the C_Q parameters do not change on lengthening the nanotube, in agreement with the trend obtained for the zigzag models and also in earlier works.

Conclusions

DFT calculations were performed to study the C_Q parameters of ^{11}B and ^{14}N atoms in SiC-doped zigzag and armchair BNNTs. The results indicate that the electronic sites of the N atoms exhibit greater effects on SiC doping than do the B atoms. Furthermore, by considering the electronegativities, doping of B and N atoms by C and Si atoms perturbs the polarity of the BNNT much more than does doping of B and N atoms by Si and C atoms. Therefore, the electronic sites of the B and N atoms of the former doped model exhibit greater changes than the latter model, compared with the pristine BNNT. Finally, comparison of the results of zigzag and armchair BNNTs reveals similar changes due to SiC doping for both nanotubes.

Computational details

DFT calculations were performed by using the Gaussian 98 package [20]. Two representative 1-nm-long structures of (6,0) zigzag and (4,4) armchair single-walled BNNT were investigated (Figs. 1 and 2). The ends of the nanotubes were saturated by hydrogen atoms. Each of the zigzag and armchair BNNT had three forms, i.e., pristine, with B and N atoms doped by C and Si atoms (Si_NC_B), and with B and N atoms doped by Si and C atoms (Si_BC_N). Initially, the structures were allowed to relax by all-atomic geometrical optimization at the BLYP exchange-functional level using the 6-31G* standard basis set. Subsequently, the electric field gradient (EFG) tensors were calculated in the optimized structures at the same level of theory. The validity of the employed level of theory and the size of the considered model to study the electronic structure of the nanotubes has been examined in earlier works [14, 15, 19]. Moreover, additional calculations were also performed on longer tubular structures of model 3 (Si_BC_N) to validate the reliability of the calculated parameters of this study according to the investigated tubular size.

The quantum-chemical calculations yielded the EFG tensors in the principal axis system (PAS) in the order: $|q_{zz}| > |q_{yy}| > |q_{xx}|$; therefore, Eq. 1 was used to evaluate the quadrupole coupling constants (C_Q). C_Q refers to the interaction energy of the nuclear electric quadrupole moment (eQ) and the EFG tensors at the site of quadrupole nucleus, which could be experimentally measured by nuclear quadrupole resonance (NQR) spectroscopy [18]. C_Q is very sensitive to the electronic site of the atom and detects any changes due to perturbations of this site. To evaluate the C_Q values for the ^{11}B and ^{14}N atoms, the standard Q values reported by Pyykkö [21] were employed in Eq. 1: $Q(^{11}B) = 40.59$ mb and $Q(^{14}N) = 20.44$ mb. The calculated C_Q parameters are presented in Tables 1 and 2 for the zigzag and armchair BNNTs.

$$C_Q(\text{MHz}) = e^2 Q q_{zz} h^{-1}. \quad (1)$$

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