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A DFT study of N-doped AlP nanotubes

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Abstract We performed density functional theory calculations for nitrogen-doped models of the representative structures of (6,0) *zigzag* and (4,4) *armchair* aluminum phosphide nanotubes (AlPNTs). Our results indicate that the optimized bond distances and tip diameters do not detect the effects of the N-doped regions; however, the effects are observed for the band gap energies and dipole moments. It is noted that substitution of the P atom by the N atom does not influence the value of band gap energy for this N-doped model. The results also indicate that the tendency of the Al atom for contribution to the Al–N bond is stronger than the tendency of the P atom for contribution to the N–P bond; therefore, the latter form of substitution makes the AlPNTs interesting as reactive materials towards other atoms or molecules, especially for the the *zigzag* AlPNT.

Keywords Aluminum phosphide nanotube · Density functional theory · Nitrogen doping

Introduction

Soon after the discovery of carbon nanotubes (CNTs) by Iijima [1], considerable efforts have been dedicated to the investigations of other types of nanotubes, among which the combinations of elements of third and fifth groups of elements (III-V) have been viewed as proper materials [2]. The CNTs are metallic or semiconductors due to the tubular diameter and chirality, whereas the nanotubes of combined atoms of third and fifth groups of elements are always semiconductors [3]. Up to now, among the possible structures of III-V nanotubes, the tubular properties of boron nitride (BN) [4], aluminum nitride (AlN) [5], gallium nitride (GaN) [6], indium nitride (InN) [7], boron phosphide (BP) [8], aluminum phosphide (AlP) [9], gallium phosphide (GaP) [10], and indium phosphide (InP) [11] have well been investigated by computational and experimental studies. It is noted that the properties of nitride compounds have been investigated more often than the properties of phosphide compounds.

We have shown in earlier studies that the properties of atomic doped nanotubes could be detected well by the calculated chemical shielding (CS) parameters [12]. Experimentally, the CS parameters are measured by nuclear magnetic resonance (NMR) spectroscopy in which quantum calculations could also reproduce reliable parameters [13]. Computations of NMR parameters are advantages of computational studies because the electronic environments of nanotubes are complex, and performing experimental NMR measurements on the nanotubes is rather difficult [14]. In this work, density functional theory (DFT) calculations are performed to investigate the properties of nitrogen-doped (N-doped) models of representative *zigzag* and *armchair* aluminum phosphide nanotubes (AlPNTs). To this aim, the structures of nanotubes are optimized and the CS parameters are calculated for the optimized structures. Due to the isoelectronic valence shells of N and P atoms, the effects of substitution of the P atom by the N atom on the properties of AlPNTs could be an important subject of study. Moreover, since the electrons of valence shell of the N atom are more than the

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Al atom, substitution of the Al atom by the N atom could make the AlPNT an *n*-type semiconductor [15].

Results and discussion

Table 1 presents the properties for the optimized structures of pristine and N-doped models of *zigzag* and *armchair* AlPNTs (Fig. 1). The pristine structures consist of 36 Al atoms and 36 P atoms in which the tips of nanotubes are saturated by the hydrogen atoms [9]. One Al atom or one P atom is substituted by one N atom to create the N_{Al} or N_P models. In comparison to the pristine models, the results indicate that the band gap energies (E_G) of both *zigzag* and *armchair* N_{Al} models, where one Al atom is substituted by one N atom, only detect the effects of dopant. However, the substitution of the P atom by the N atom, in which the valence shells of the N and P atoms are isoelectronic, has no effect on the values of E_G of the *zigzag* and *armchair* N_P models of AlPNTs. Slight changes are observed for the values of dipole moments (μ) for the N-doped models in which the changes are more notable for the N-doped *armchair* AlPNTs because their initial zero values are changed. The values of bond distances (d) and tip diameters (d_{Tip}) of the N-doped models are not changed with respect to the pristine models.

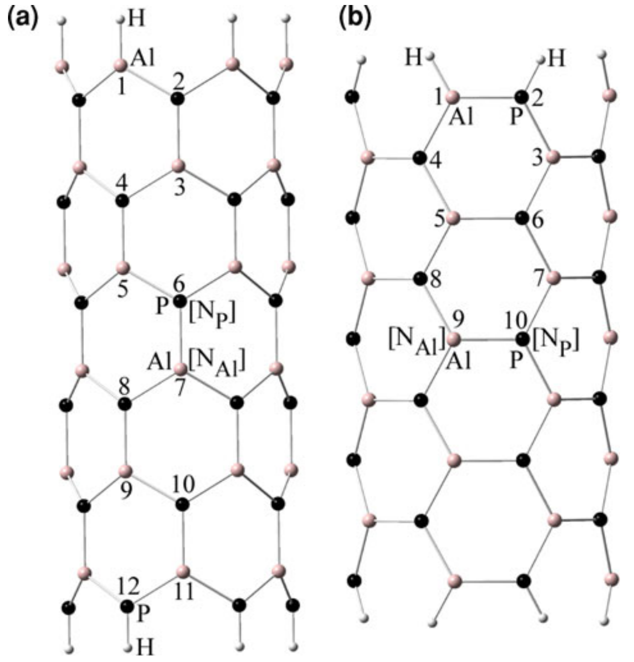

Fig. 1 The *zigzag* model (**a**) and the *armchair* model (**b**) of the AlPNT. The N-doped atoms are indicated by the *brackets*

The calculated CS parameters consisting of isotropic and anisotropic chemical shielding parameters (CS^I and CS^A) for the ^{15}N, ^{27}Al, and ^{31}P atoms of pristine and N-doped *zigzag* models are listed in Table 2. The results are presented as the averaged values for atoms of each layer based on the similarities of the CS parameters for atoms of each layer. The results reveal that the CS parameters for atoms of the tips of N-doped nanotubes, Al_1 and P_{12}, do not detect the effects of the N-doped region; however, notable changes are observed for some of the other atoms. In the N_{Al} model, where one Al atom is substituted by one N atom, the CS parameters for atoms of the Al_5, Al_7, and Al_9 layers detect the slight changes of the N-doped region. However, the changes of the CS parameters for atoms of the P_4, P_6, and P_8 layers of the N_{Al} model detect more notable effects with respect to the pristine model. There are three N–P bonds instead of Al–P bonds in the N_{Al} model where the CS parameters for atoms of the P_6 and P_8 layers, which are directly bonded to the N atom, detect the most significant changes among other atoms. The values of CS^I parameters for the P atoms of these two layers are decreased, whereas the values of their CS^A parameters are increased in comparison to the pristine model. In the N_P

Table 1 Optimized properties

Property	*Zigzag* AlPNT			*Armchair* AlPNT		
	Pristine	N_{Al}	N_P	Pristine	N_{Al}	N_P
E_G (eV)	3.03	2.14	3.04	3.87	2.94	3.87
μ (Debye)	6.93	7.21	7.01	0	0.53	0.53
$d_{Al–P}$ (Å)	2.31	2.31	2.31	2.31	2.31	2.31
$d_{Al–H}$ (Å)	1.58	1.58	1.58	1.58	1.58	1.58
$d_{P–H}$ (Å)	1.42	1.42	1.42	1.42	1.42	1.42
$d_{Al–N}$ (Å)	–	–	1.84	–	–	1.84
$d_{N–P}$ (Å)	–	1.80	–	–	1.79	–
$d_{Al–tip}$ (Å)	7.00	7.00	7.00	–	–	–
$d_{P–tip}$ (Å)	8.10	8.09	8.10	–	–	–
d_{Tip} (Å)	–	–	–	8.52	8.39	8.46

See Fig. 1 for the models

E_G Band gap energy, μ dipole moment, d distance

Data for pristine model are from Ref. [9]

Table 2 CS properties for *zigzag* AlPNT

Al atom	Pristine	N_{Al}	N_P	P atom	Pristine	N_{Al}	N_P
1	345; 120	345; 121	345; 120	2	488; 193	487; 194	488; 197
3	342; 78	342; 78	341; 84	4	485; 120	483; 132	483; 117
5	347; 82	344; 101	363; 66	6	489; 125	424; 162	488; 122
7	346; 79	347; 96	354; 78	8	486; 124	376; 210	492; 123
9	346; 74	353; 82	345; 73	10	501; 167	504; 161	500; 168
11	314; 133	315; 129	314; 133	12	513; 96	512; 98	513; 97
N	–	273; 160	101; 110	–	–	–	–

See Fig. 1a for the models, where the Al atoms are designated by odd numbers and the P atoms are designated by even numbers. In each row, the first value is for CS^I and the second value is for the CS^A parameter (ppm) for *zigzag* models. Data for the pristine model are from Ref. [9]

model, where one P atom is substituted by one N atom, there are three Al–N bonds instead of three Al–P bonds. In this model, the CS parameters for the P atoms do not detect the effects of the N-doped region, but some slight changes are observed for the atoms of Al_5 and Al_7 layers in which the values of CS^I parameters are increased, whereas the values of CS^A parameters are deceased with respect to the pristine model. The trend means that the tendency of the Al atom for contribution to the Al–N bonding is more than this tendency for contribution to the Al–P bonding. The difference of electronegativity between the Al and N atoms is larger than between the Al and P atoms; therefore, the trend could well be proven. The CS parameters for the N atoms in the N_{Al} and N_P models also indicate that the N atom is proper for the Al–N bond than the N–P bond. According to these observations, it could be suggested that the N_{Al} model is a more reactive material than the pristine and the N_P models of the *zigzag* AlPNT.

Table 3 shows the CS parameters for ^{15}N, ^{27}Al, and ^{31}P atoms of the pristine and the N-doped models of (4,4) *armchair* AlPNT (Fig. 1b). Parallel to the results of the *zigzag* models, the CS parameters for atoms of Al_1 and P_2 layers, which are located at the tips of nanotubes, do not detect the effects of the N-doped region with respect to the pristine model. In the N_{Al} model, the changes of the CS parameters for atoms of the P_6, P_8 and P_{10} layers indicate the small tendency of the P atom for contribution to the N–P bond, where the values of CS^I parameters are decreased but the values of CS^A parameters are increased in comparison to the pristine model. The CS parameters for atoms of the Al_5, Al_7, and Al_9 layers also detect notable changes with respect to the pristine model. In the *armchair* N_P model, where one P atom is substituted by one Al atom, the changes of the CS parameters for the atoms of Al_7 and Al_9 layers detect notable changes, but slight changes are observed for the atoms of the P_8 and P_{10} layers. Comparing the CS parameters for the N atoms also indicates that the N atom is proper for the Al–N bond in the N_P model more than the N–P bond in the N_{Al} model. Parallel to the results of *zigzag* models, the N_{Al} model of the *armchair* AlPNT could also be expected to be a reactive material towards other atoms or molecules.

The CS parameters for the N atoms indicate that the electrons of N atoms are not shared within the N–P bonds in the N_{Al} models, but the electrons are shared within the Al–N bonds in the N_P models. The trend is in agreement with the trends obtained by the CS parameters for the Al and P atoms of the *zigzag* and *armchair* AlPNTs. Moreover, the larger values of CS parameters for the N atom of the *zigzag* model than the values of CS parameters for the N atom of the *armchair* model indicate that the *zigzag* N_{Al} model could be expected to be a more reactive material than the *armchair* N_{Al} model and all other models of the AlPNT.

Table 3 CS properties for *armchair* AlPNT

Al atom	Pristine	N_{Al}	N_P	P atom	Pristine	N_{Al}	N_P
1	332; 134	332; 132	332; 133	2	531; 109	529; 109	530; 110
3	337; 88	337; 90	337; 89	4	504; 179	507; 176	504; 180
5	356; 70	354; 77	354; 75	6	524; 116	521; 136	523; 109
7	353; 67	348; 94	365; 58	8	512; 110	447; 152	516; 93
9	356; 69	354; 76	367; 58	10	513; 106	423; 171	514; 110
N	–	250; 47	110; 100	–	–	–	–

See Fig. 1b for the models where the Al atoms are designated by odd numbers and the P atoms are designated by even numbers. In each row, the first value is for CS^I and the second value is for the CS^A parameter (ppm) for *armchair* models. Data for the pristine model are from ref. [9]

Conclusions

Our DFT calculations indicate that the bond distances and tip diameters do not detect the effects of the N-doped region. The band gap energies and dipole moments detect the effects of the N-doped region; however, the band gap energies of the N_P models, where the P atom is substituted by the N atom, are not changed in comparison to the pristine models. The CS parameters for the Al and P atoms close to the N-doped regions detect significant changes in comparison to the pristine models where the effects are more obvious for the N_P models. The results indicate that the tendency of the Al atom for a contribution to the Al–N bond is higher than the tendency of the P atom for contribution to the N–P bond. And as the final trend, the *zigzag* N_{Al} model of AlPNT could be expected to be the most reactive material among all possible models of the *zigzag* and *armchair* AlPNTs.

Computational details

DFT calculations were carried out to investigate the hydrogen-saturated N-doped models of representative (6,0) *zigzag* and (4,4) *armchair* AlPNTs employing the B3LYP method and the 6-31G* standard basis set as implemented in the Gaussian 98 package [16]. The N-doped models were created by substitution of one Al atom or one P atom by one N atom where the N_{Al} model stands for the substitution of the Al atom by the N atom and the N_P model stands for the substitution one P atom by one N atom (Fig. 1). During the optimization process, all-atomic geometries were allowed to relax, and the CS parameters were then calculated for the optimized structures employing the gauge included atomic orbital approach (GIAO) [17]. Equations 1 and 2 were used to convert the calculated CS tensors, which are in the principal axes system (PAS), to isotropic and anisotropic CS properties (CS^I and CS^A). Table 1 presents the optimized properties, and Tables 2 and 3 present the CS properties for the N-doped models of AlPNT. The available data for the pristine AlPNTs are also included in the tables from a recent study [9].

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

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

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