Density Functional Theory Studies of Defects in the (5,5) Silicon Nanotube

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ABSTRACT

We have performed density functional theory (DFT) calculations to investigate the properties of defect in a representative armchair model of silicon nanotubes (SiNTs). To this aim, the structures of pristine and defective (5,5) SiNTs have been optimized and the properties such as bond lengths, total energies, binding energies, formation energies, gap energies, and dipole moments have been evaluated for the optimized structures. The results indicate that the evaluated properties could yield the effects of the defect on the properties of pristine SiNT.

Keywords: Silicon; Nanotube; Defect; Density functional theory

INTRODUCTION

Soon after the discovery of carbon nanotube (CNT) by Iijima [1], numerous researches have been dedicated to investigate the properties and applications of this novel material [2,3]. Moreover, substitutions of CNTs by other types of nanotubes have become topic of several researches [4,5]. Among them, the stabilized structures and properties of silicon nanotubes (SiNTs) have been successfully confirmed by computations and experiments [6,7]. It is noted that the valence shells of carbon and silicon atoms are iso-electronics which could make possible the substitutions of CNTs by SiNTs. Previously, this type of atomic substitution of nanotubes has been introduced as an important topic of research [8].

In addition to the stable pristine structures of nanotubes, investigating the properties of possible defect in there is an important task [9]. It is well known that the structural defects could happen during the synthesizing process in which they could be well investigated by doing calculations. In this work, we have investigated the effects of defect on the properties of the representative (5,5) armchair SiNT by doing density functional theory (DFT) calculations in the pristine and defective nanotubes (Fig. 1). To make

possible the traceless concentration of the defective region, we have removed one silicon atom from the pristine nanotube and then we have investigated the resulting structure and compared with the properties of pristine model.

METHOD

Within this work, we have performed DFT calculations at the levels of the B3LYP and the BLYP exchange-correlation functionals and the 6-31G* standard basis set which are initially implemented in the Gaussian 98 package of program [10-13]. The pristine model of the representative (5,5) armchair SiNT contains 110 silicon atoms and 20 hydrogen atoms (Fig. 1a). To make the defective model, one silicon atom is removed from the center of the nanotube to make the defective SiNT including 109 silicon atoms and 20 hydrogen atoms (Fig. 1b). It is important to note that the hydrogen atoms are used to saturate the open tips of nanotubes to avoid the dangling effects in the molecular calculations [14]. The geometries

of both structures have been fully optimized and the structural properties of bond lengths, total energies (E_T), binding energies (E_B), formation energies (E_F), gap energies (E_G), and dipole moments (D_M) have been evaluated for the optimized structures (Table 1). The formula, which is used to evaluate the binding energy, is $E_B = (E_{NT} - mE_{Si} - nE_H)$, in which m designates the numbers of silicon atoms and n designates the numbers of hydrogen atoms of nanotubes. The formula, which is used to evaluate the formation energy, is $E_F = E_{Defective-SiNT} + E_{Si} - E_{Pristine-SiNT}$. Gap energy is also obtained by the difference of energies between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) by the formula of $E_G = E_{LUMO} - E_{HOMO}$.

RESULTS AND DISCUSSION

The investigated models of the (5,5) armchair SiNT are shown in Fig. 1 (panel a shows the pristine model and panel b shows the defective model). A quick look at the results of Table 1 of the two employed computational methods including total energies (E_T), formation energies (E_F), binding energies (E_B), gap energies (E_G), and dipole moments (D_M), reveals that the obtained parameters are different based on different theoretical levels of computations [10-12]. However, the orders of changes are similar in both models which satisfy our goal of study. Indeed, comparing the properties of the pristine and the defective SiNTs is the major goal of this study which could be satisfied by the obtained parameters of the two levels. Not to mess discussion, we would

refer to the values obtained by the B3LYP/6-31G* level of computations through the following text.

Different values of total energies are calculated for the pristine and defective models of SiNT because the models have different numbers of electron and structural deformations are also occurred in the defective model. By removing one silicon atom from the structure to make the defective model, two pentagonal rings are appeared in the structure of optimized nanotube. It could be seen (Fig. 1) that the values of bond lengths at the region of the defect site are significantly changed due to formation of the pentagonal rings but the values of other bond lengths do not detect notable changes with respect to the pristine SiNT. Moreover, the values of formation energies also indicate that the formation of the defective structure needs some magnitude of energy. The pristine model has one silicon atom more than the defective model of SiNT and all the constructing rings of the nanotube are hexagonal in the pristine model whereas there are two pentagonal rings instead of two hexagonal rings in the structure of defective nanotube. With respect to the values of binding energies, these properties reveal that the formation process of the pristine model releases more energy than the formation process of the defective model of SiNT revealing that the pristine model could be considered as the preferred structure of the two investigated formation processes of SiNT. Indeed, this trend could be well confirmed by the properties of different kinds of energies which are obtained by DFT calculations for the pristine and the defective models of the investigated SiNT.
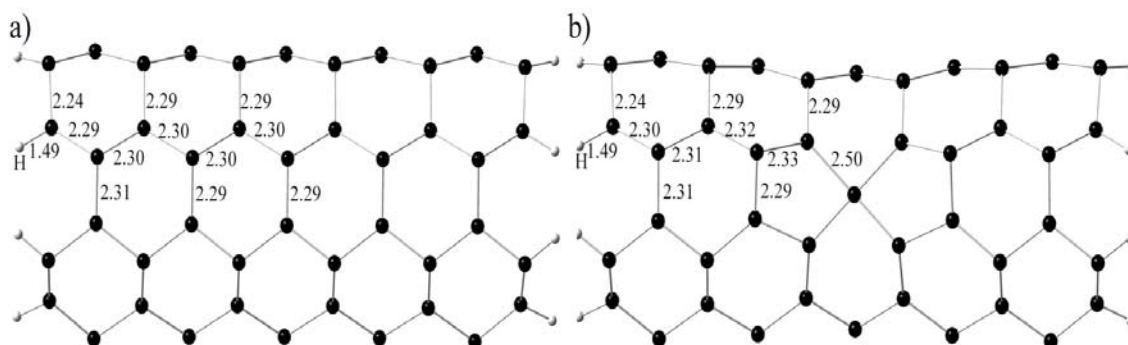

Fig. 1. The 2D views of (a) the pristine and (b) the defective models of SiNTs. The values of optimized bond lengths are written on the selected bonds.

Table 1. The structural properties *

Property	Pristine	Defective
E_T	- 866876	- 858996
	[- 866822]	[-858942]
E_F	—	5.62
	[—]	[6.07]
E_B	-422	-416
	[-420]	[-414]
E_G	1.14	0.79
	[0.55]	[0.25]
D_M	0.01	0.65
	[0.01]	[0.83]

* The units of energies and dipole moment are eV and Debye respectively. The results out of brackets are obtained by the B3LYP/6-31G* level and the results in the brackets are obtained by the BLYP/6-31G* level.

The values of gap energies, which refer to the conducting properties of matters, indicate that the value is smaller for the defective model with respect to the pristine model of SiNT. This trend means that the defective model could be considered as a better conductor than the pristine model of SiNT. Moreover, a look at the values of dipole moments, which refer to the polarity of matters, indicates that the polarity of the defective model is much more than the polarity of the pristine model of SiNT. The magnitude of dipole moment of SiNT is significantly increased due to defects in the structure of nanotube. Interestingly, the values of gap energies and dipole moments confirm that the defective SiNT could be considered as a more reactive material than the pristine model due to having smaller value of gap energy and larger value of dipole

moment than the pristine model. In parallel to the results of different kinds of energies, which revealed that the formation of pristine model is much more preferred than the defective model, the results of gap energies and dipole moments also confirm that the pristine model could be considered as a much more stable material than the defective SiNT.

CONCLUSION
The values of structural parameters obtained by DFT calculations for the pristine and defective models of the (5,5) armchair SiNT indicated that the formation process of the pristine model could be preferred more than the defective model. The pentagonal rings of the defective model, which are formed by removing one silicon atom from the pristine SiNT, cause changes to the properties of the investigated nanotube. The obtained values of gap energies and dipole moments indicated that the conducting property and the polarity of the defective model are more than the pristine SiNT. The trend reveals that the defective model could be considered as a reactive material in comparison o the pristine SiNT. As the final remarks, the defect brings new properties of less stability, more conductivity and more polarity for the investigated SiNT.

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