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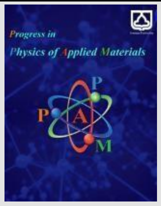

Electronic structure engineering of diamond nanowires by studying the effects of substitution and growth orientation

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ABSTRACT

In this paper boron doped carbon nanowires have been studied by density functional theory (DFT) with the help of hybrid approximation. The morphology of the studied carbon nanowires with diamond structure, was cylindrical with [100], [110], and [111] growth directions. The carbon atoms on the lateral surfaces were saturated by hydrogen atoms. The results showed that the band gap energy of carbon nanowires has decreased compared to bulk diamond by reducing the quantum dimensions to one dimension. Then the effect of boron atom substitution was studied. The calculation results revealed that changing the growth direction causes interesting behaviors in the study of atomic substitution. Hence, using boron atom dopants are very important in increasing the density of electronic states in [100] and [110] directions. Substitution and change in growth direction caused a change in the position of the Fermi level. Boron substitution in [110] carbon nanowire caused the metallization of the structure, for the nanowire with [111] growth direction it caused a change in semiconductor type, and for the nanowire with [100] growth direction it caused the band gap energy to decrease.

1. Introduction

Among the carbon allotropes, diamond has received special attention from industry due to its special characteristics, including good thermal conductivity and high mechanical strength. Due to having a wide energy gap, high mobility of electrons and holes, and being electrophilic, diamond can be used in ultraviolet light detectors, field effect transistors, etc.

Also, according to the recent discovery of many forms of carbon, from C60 and carbon nanotubes (CNTs) to graphene, researchers believe that other crystallographic forms of carbon can show special properties [1,2].

One of the most important reasons for the appearance of special properties in nanostructures is the large surface-to-volume ratio. At the nanoscale, in nano dimensions, the behavior of materials is changed and the behavior of surfaces overcomes the behavior of its mass (volume). In fact, on nano dimensions it will be possible to control the inherent properties of the material, including electrical properties, melting temperature, magnetic properties, and even the color of the material, etc., without changing the chemical composition of the material [3].

It is believed that carbon nanostructures will play an important role in nanotechnology and nanomaterials. Meanwhile, one-dimensional carbon nanostructures (such as nanowires and nanotubes) have received special attention [4]. While nanowires geometrically extend only in one direction, here the most important and influential factor in the occurrence of special electronic, optical, magnetic, and chemical properties is influenced by the unique behavior of the carbon atom in the structure. Also, the electronic structure is influenced by the effect of quantum confinement, growth orientation, and high surface-to-volume ratio [5, 6].

Due to the fact that bulk diamond has special properties such as negative electronegativity, thermal conductivity, and high mechanical strength, few studies and researches have been done on diamond nanowires compared to other nanowires such as silicon nanowires [7,8].

Recently, in the study of the mechanical properties of carbon nanotubes and nanowires with a diamond structure, Shendrova et al [9] showed that these nanowires have

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better mechanical properties and are more stable in terms of energy compared to carbon nanotubes of the same diameter. Therefore, it can be said that the synthesis of carbon nanowires is less complicated than carbon nanotubes. It was also found that the mechanical properties of these one-dimensional nanostructures are also dependent on the cross-section radius and growth direction [10].

In the article of Monavari et al. [11], phononic, vibrational, and optical properties of carbon nanowires with diamond structure in [110] direction were investigated by DFT. The positive phonon frequencies indicated the stability of the structure and the ability to construct it in the field of experimental physics.

Also, studies on the energy band gap of diamond nanowires have been carried out by Barnard et al. [12] and critical factors such as wire diameter, surface morphology, and surface hydrogenation have been found to reduce the energy band gap.

Solano investigated the effects of structure and anisotropy of diamond nanowires, in [001] and [111] directions, on its electronic properties. It was shown that [001] nanowires have more band gap than [111] nanowires, which is due to the quantum confinement effect [13]. There are several reports on the synthesis of diamond nanowires, which have investigated the development and manufacturing methods of these materials [14]. Among these, two methods of reactive ion etching (RIE) and chemical vapor deposition (CVD) can be mentioned [15,16]. In the report of Peng et al. [17], experimental applications are mentioned, such that carbon nanowires doped with boron atoms are used as a sensor and absorber of carbon monoxide molecule as a gas sensor.

In this research, with the help of the density functional theory (DFT), the effect of the orientation and substitution of boron atoms on the energy and density of electronic states has been investigated. We investigated the change of electronic properties of carbon nanowire saturated with hydrogen atoms (named as DNw:H) when substituted with boron atoms (named as BDNw:H) in three growth directions. The results of our research show that the electronic properties of carbon nanowire with a diamond structure are strongly influenced by the growth orientation and substitution with boron atoms. Our results show that the substitution of boron in [100], [110], and [111] diamond nanowires cause a change in the type of semiconductor, conductivity, and reducing the energy gap of the system. Therefore, the results of this research can have high applications in transistors and other electronic devices.

2. Calculation method

The optimization method of carbon nanowire saturated with hydrogen in local density approximation (LDA) using plane wave pseudo-potentials has been carried out with the help of Quantum-espresso computing package. It was found that in order to converge the total energy around 1 meV, the required cutoff energy is 30 Ha (Fig. S1). The first Brillouin zone is meshed in the form of 1×1×12 by the Monkhorst-Pack grids mesh method after performing the energy convergence test up to 5 meV [11,18]. It should be noted that the LDA, Troullier-Martin (TM) pseudo-potential was used in the calculations [19].

In performing the calculations, the contribution of van der Waals interactions in solving Kohn-Sham equations with the self-consistent field is considered. We used semi-empirical van der Waals correction method of Grime D2 type with optional London variables [20,21].

In all three growth directions [100], [110], and [111], the optimization steps for boron substitution were carried out in the same conditions as mentioned above.

The nanowires were designed with a cross section of 0.74 nm. The bond type between the carbon atoms in the diamond structure is sp^3 hybridized, and all the carbon atoms have single free bonds at the edge of the structure. In order to form sp^3 hybridization and the formation of a diamond structure, only hydrogen atoms that have a shared single bond can be used. In fact, it can be said that the carbon structure is saturated with hydrogen atoms at the edges that have dangling bonds.

3. Results and discussion

In this section, the effect of boron dopant on the electronic properties of hydrogen-saturated diamond nanowires grown in the [110] direction was studied using initial calculations. The optimized structure of hydrogen-saturated diamond nanowires in three growth directions is shown in Fig. 1. The orange, white, and pink spheres correspond to carbon, hydrogen, and boron atoms, respectively.

Following numerical calculations and structure optimization, the average length of bonds (C-C, C-H, and C-B), the energy of the highest filled level in the valence band (V), the lowest unoccupied level in the conduction band (C), E_{gap}, the band gap energy, and N the number of all atoms present in the structure are reported in Table 1. The calculated C-C bond length is consistent with the findings of Barnard et al. [22].

The band gap energy related to the bulk diamond lattice was calculated to be 5.491 eV after performing electron calculations [23]. While the energy gap of pure nanowires in three growth directions [100], [110], and [111] decreased respectively to 1.768 eV, 2.853 eV, and 1.793 eV compared to bulk diamond. Also, according to the quantum confinement effect, it is expected that the energy gap of carbon nanowire is more than bulk diamond. In fact, hydrogen atoms have created surface levels inside the band gap energy and thus the band gap energy of carbon nanowire has become smaller than that of bulk diamond in all growth directions.

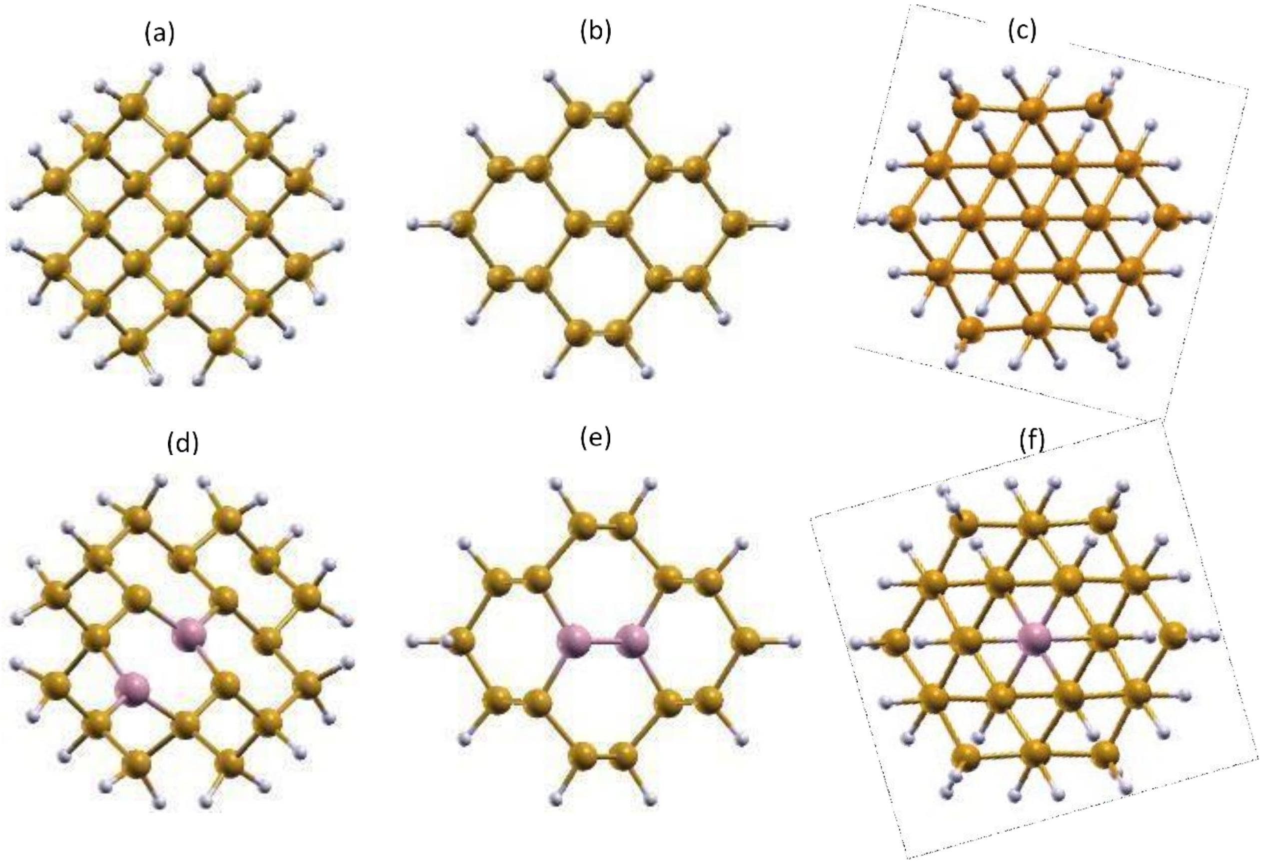

Fig. 1. (a-c) configuration of the optimized geometrical structure of the cross section of the carbon nanowire saturated with hydrogen atoms (DNw:H) in three growth directions [100], [110], and [111], respectively. (d-f) Optimized geometry structure configuration of boron substitution unit cell in carbon nanowire saturated with hydrogen atom (BDNw:H) in three growth directions.

Table 1. Structural characteristics and band gap of pure carbon nanowires (DNw:H) and substituted with boron atoms (BDNw:H).

Geometry		N	C-C	C-H	C-B	V (eV)	C (eV)	Egap (eV)	Egap (eV) [17,18]
[100]	DNw:H	41	1.543	1.104	--	-0.554	3.169	3.723	3.76
	BDNw:H		1.550	1.106	1.597	-0.523	1.185	1.708	--
[110]	DNw:H	28	1.549	1.112	--	-1.882	0.756	2.638	--
	BDNw:H		1.557	1.109	1.585	--	--	metal	--
[111]	DNw:H	49	1.539	1.110	--	-3.247	0.451	3.698	3.51
	BDNw:H		1.554	1.095	1.564	-0.498	1.712	2.210	--

The calculated band structures for DNw:H and BDNw:H are shown in Fig. 2. The position of the Fermi level in the pure structures shows that carbon nanowires with [110] and [111] growth directions are n-type semiconductors. Although the growth direction [100] of the Fermi level is close to the valence band, and also, among other results obtained in this study, we can refer to the discovery of p-type semiconductor, which is according to the findings of Barnard et al. [24].

Substitution of boron inside the diamond nanowire structures by creating an inter-gap level, a further reduction of the energy gap is observed compared to the pure state. Also, according to Fig. 2) b(, the displacement of the position of the Fermi level shows the changes in the electronic properties. The changes are such that the substitution of boron in the (110) carbon nanowire caused the metallization of the structure, for the nanowire with the [111] growth direction.It caused the semiconductor state to change from n to p-type, and led to decrease energy gap for the nanowire with the growth direction of [100]. In fact, it can be said that the change in the electronic structure of carbon nanowires is the result of the interactions of boron atoms' electrons with carbon atoms of nanowires. Also, changing the arrangement of carbon atoms in three growth directions [100], [110], and [111], and changing the type of interaction with the boron atom can be considered as the main factor in changing the electronic structure.

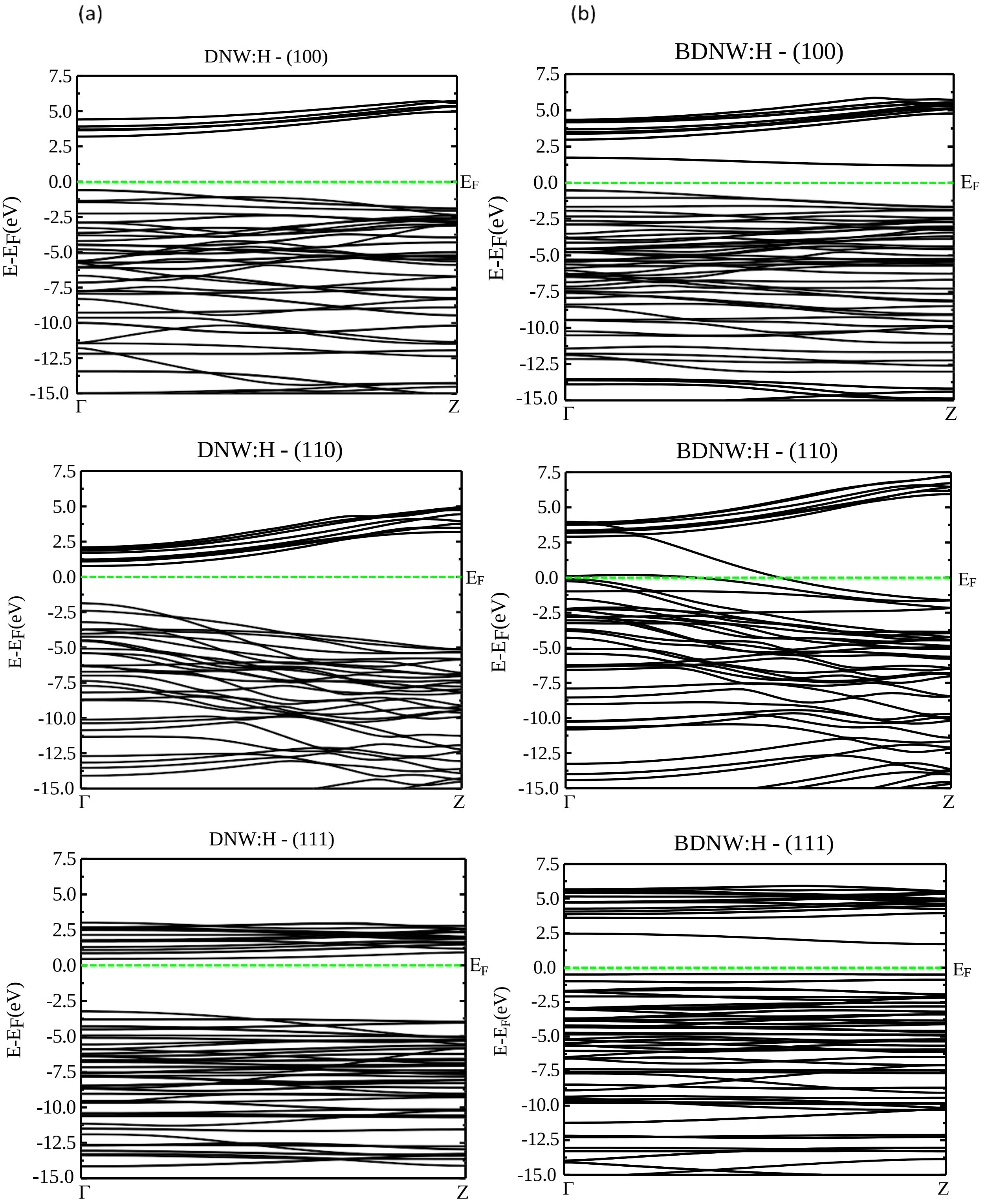

Fig. 2. Band structure of (a) pure carbon nanowires (DNw:H), (b) carbon nanowires substituted with boron (BDNw:H) in different growth directions.

In this part, it used special-colored bands with minimum and maximum values of 0 and 1 for the orbitals of each type of atom in the band structure, which shows the contribution of pure and boron-doped nanowires in three directions. k-resolved density of states (Fig. 3) shows that with changes in the energy band from black to yellow, it indicates an increase in the contribution of the electron density. Also, the contribution of the density of electron states in the bands far from the Fermi energy in the valence band is related to the s orbital of carbon atoms, while the contribution of the p-orbital of carbon atoms in the density of band states is higher in the band close to the gap, so the semi-occupied levels are more effective in material conductivity.

Our results showed that the contribution of intragap level density in all three growth orientations is related to the s and p orbitals of boron atoms and the contribution of hydrogen atoms is more evident in the conduction bands. This issue is shown in Fig. 3, which is related to the contribution k-resolved density of states for pure and boron-doped carbon nanowires.

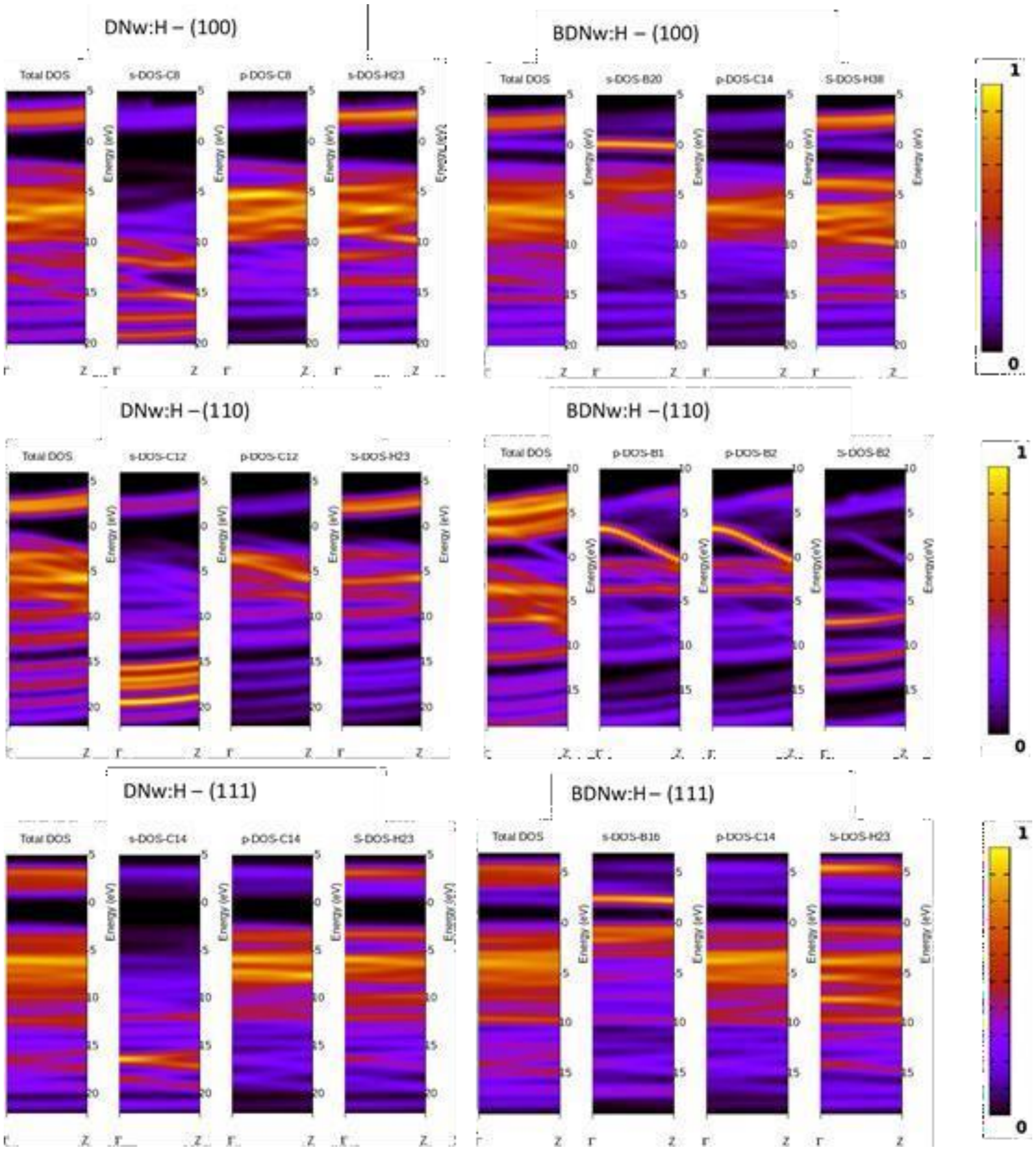

Fig.3. k-resolved density of states for pure and B doped diamond nanowires with different growth directions.

The preliminary results of calculations have shown that with boron doping, the electronic density of states (DOS) increases in all three growth directions [100], [110], and [111]). Also, for the growth directions [100] and [111], an intragap level is formed between the last full level in the valence band and the first empty level in the conduction band. Thus, the boron impurity for the diamond nanowire in the [110] direction caused the instability of the Fermi level and metallization of the structure. This is shown in Fig. 4. The density of electron states of the conduction band levels is much lower than the valence band levels.

As shown in Fig. 4, the density of electron states of carbon nanowire saturated with hydrogen (DNw:H) and substituted with boron (BDNw:H) is increasing in [100], [110], and [111] orientations, respectively.

Also, our results in Supplementary information (Fig. S2) indicate that the change in growth direction in diamond nanowires causes changes of the electronic density of state. This issue is due to the fact that with cylindrical cutting of the bulk diamond structure in three different growth directions [100], [110], and [111], the number of atoms obtained in the simulation of unit cell with the same radius increases correspondingly. find This has caused the density of electronic states to increase.

As mentioned earlier, the interactions of the boron atomic p orbital electrons with the central carbon atom electrons of the structure in three growth orientations with the formation of intergap levels cause the changes in electronic properties (metal, n and p type semiconductors). In nanowires, the formation of these levels increases the overall density of states of boron-doped nanowires.

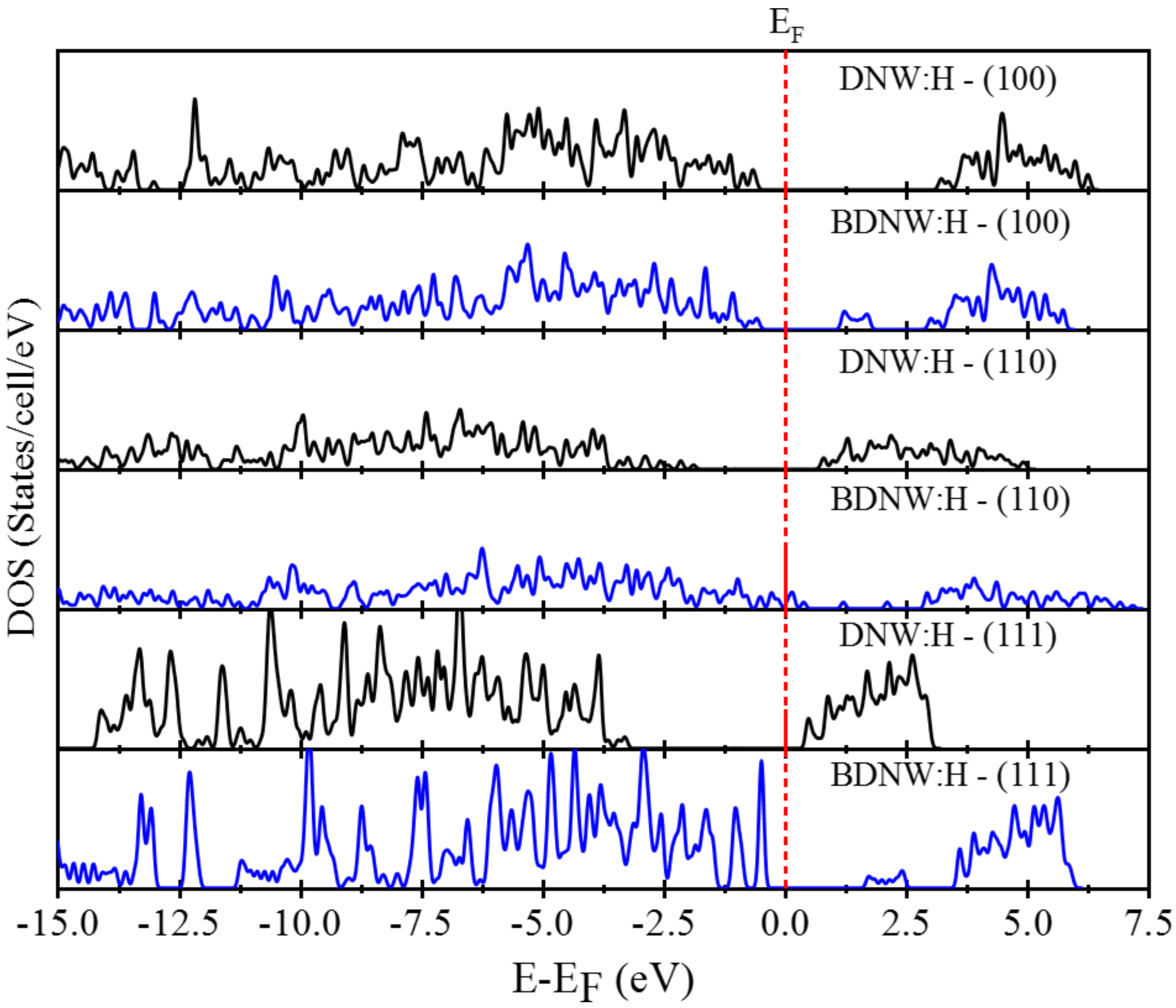

Fig.4. DOS related to pure carbon nanowires (DNw:H) and substituted with boron atoms (BDNw:H) in three growth directions.

4. Conclusion

Our results showed that the energy gap of carbon nanowire saturated with hydrogen in all three directions of growth compared to bulk diamond has decreased significantly and caused the nanowires to become semiconducting. This change is due to the formation of surface levels caused by hydrogen atoms in such a way that the energy gap of carbon nanowire is smaller than the energy gap of bulk diamond under the influence of surface effects.

Also, the effect of substitution of carbon nanowires in three growth directions [100], [110], and [111] with boron atoms was investigated and it was determined that boron substitution has significant effects on the band structure of nanowires. The study of the band structure of boron-doped carbon nanowire shows that the substitution of boron atom causes the electron density to increase and the formation of inter-gap levels, so that in the growth direction [100] a decrease in the energy gap is observed correspondingly. The growth direction [111] changes the semiconductor type of nanowire from n to p type, and for the growth direction [110] the structure is metalized. This nano technology can be used especially in the industries related to the design of field effect transistors, n-p junctions and especially the construction of mechanical-electronic sensors.

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