

CHARACTERISTIC PHYSICAL PROPERTIES OF B-DOPED GERMANENE NANORIBBONS: A DFT STUDY

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ARTICLE INFO		ABSTRACT
Received:	01/8/2022	This work studies one-dimensional germanene materials (germanene nanoribbons (GeNRs)) when doped with B atoms. The doped structure and electromagnetic properties of the pre-and post-doping systems will be studied and investigated. There are two doping ratios studied, B:Ge=1:2 and B:Ge=1:3. With the four configurations studied, the configurations are stable and retain the hexagonal honeycomb structure after doping. The theory used for research is density functional theory (DFT), combined with VASP software to simulate materials on a high-performance computer system. Research has shown that configuration 1-2(2) has a band gap extended to 0.585eV, thus this configuration has potential application in room temperature field transistors. The s-p multi-orbital hybridization, charge distribution, and displacement in the doped configurations will also be studied in detail. The research opens up future applications in the fields of nanoelectronics and semiconductor technology.
Revised:	16/9/2022	
Published:	16/9/2022	
KEYWORDS		
Germanene nanoribbons		
Boron doping		
Doping configuration		
Configurations		
One-dimensional material		

CÁC TÍNH CHẤT VẬT LÝ ĐẶC TRƯNG CỦA CÁC BĂNG NANO GERMANENE MỘT CHIỀU ĐƯỢC PHA TẠP B: MỘT NGHIÊN CỨU DFT

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THÔNG TIN BÀI BÁO		TÓM TẮT
Ngày nhận bài:	01/8/2022	Công trình này nghiên cứu vật liệu germanene một chiều (băng nano germanene (GeNRs)) khi được pha tạp các nguyên tử B. Cấu trúc và đặc tính điện tử của hệ trước và sau pha tạp sẽ được nghiên cứu và khảo sát. Có hai tỷ lệ pha tạp được nghiên cứu: B: Ge = 1: 2 và B: Ge = 1: 3. Với bốn cấu hình được nghiên cứu, các cấu hình ổn định và giữ được cấu trúc tổ ong lục giác sau khi pha tạp B. Lý thuyết được sử dụng để nghiên cứu là lý thuyết phiếm hàm mật độ (DFT), kết hợp với phần mềm VASP để mô phỏng vật liệu trên hệ thống máy tính hiệu năng cao. Nghiên cứu đã chỉ ra rằng cấu hình 1-2 (2) có độ rộng vùng cấm mở rộng đến 0,585eV, do đó cấu hình này có tiềm năng ứng dụng trong các bóng bán dẫn trường ở nhiệt độ phòng. Sự lai hóa đa quỹ đạo s-p, sự phân bố và dịch chuyển điện tích trong các cấu hình pha tạp cũng sẽ được nghiên cứu chi tiết. Nghiên cứu mở ra các ứng dụng trong tương lai trong lĩnh vực điện tử nano và công nghệ bán dẫn.
Ngày hoàn thiện:	16/9/2022	
Ngày đăng:	16/9/2022	
TỪ KHÓA		
Germanene một chiều		
Pha tạp boron		
Cấu hình pha tạp		
Các cấu hình		
Vật liệu một chiều		

DOI: <https://doi.org/10.34238/tnu-jst.6313>

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1. Introduction

The role of science and nanotechnology cannot be denied, this technology creates compact and sophisticated devices for human life. Low-dimensional materials have their own characteristics and properties, and the size limitation causes their physical properties to change. When the particle moves in three-dimensional space, the particle's energy is continuous, but when the particle is confined, the particle's energy is interrupted. The best known two-dimensional material is graphene with a honeycomb lattice formed from C atoms [1]. Graphene is a two-dimensional material with flat structure, high electrical conductivity, high thermal conductivity, high elasticity, high stiffness and flexibility [2] – [6]. Graphene rivals materials such as silicene and germanene [7]. Silicene and germanene both have a hexagonal honeycomb structure like graphene, the big difference being that their structure is not as flat as that of graphene [8] – [11]. Studies on successful synthesis of germanene have been conducted since 2014, followed by other works synthesizing single-layer germanene with a thickness of one atom [12] – [15]. Both graphene, germanene and silicene share many similar characteristics, ranging from s , p_x , p_y , p_z multi-orbital hybridizations to other electronic properties. The electrons in the Brillouin region, near the K, K' points, act as massless relativistic particles [16]. The structural and electronic properties of germanene have been extensively studied using first principle calculations [17] – [23]. DFT calculations have shown that the buckling of germanene is in the range of 0.64-0.74 Å [22], the reason for such a difference is that different calculation schemes will give different values. The one-dimensional structures of germanene are called germanene nanoribbons (GeNRs), and the size restriction gives rise to very different structural properties and properties of GeNRs compared with two-dimensional systems [24], [25]. The appearance of modified hydrogen atoms at the two edges of GeNRs has given rise to a small band gap, the purpose of doping foreign atoms into GeNRs to expand its band gap and create substances that can be applied. used under specific conditions [11], [26]. In this work, B atoms will be doped in GeNRs with two ratios B:Ge=1:2 and B:Ge=1:3. The electromagnetic properties of the pre- and post-doping systems will be studied and compared to find out the differences.

2. Methods

Using density functional theory (DFT) combined with VASP software to simulate the electromagnetic properties of materials before and after doping. VASP software will be used on a high-performance computer system to simulate the physical and chemical processes that take place when doping B into GeNRs. The stability as well as the structural properties of the system will be found in the output files of the VASP.

The split point grid in the KPOINTS files will be set at 1 1 11, after optimization, the split points will be increased to 1 1 100 to calculate the energy band structure and state density of the system. The cutoff energy during the study was set at 500eV. The Projector-Augmented Wave (PAW) pseudopotentials is used to describe the interaction potentials on the electrons in the system.

3. Geometric structure

The unit-cell configuration of the pristine system (Figure 1a) and the doped systems (Figure 1b-e) shows the position of the substitution doped B atoms (green atoms) in the GeNRs system. Figure 1b and Figure 1c correspond to the doping ratio B:Ge=1:2; Figure 1d and Figure 1e correspond to the doping ratio B:Ge=1:3. All doping configurations are stable and retain the honeycomb hexagonal structure after optimization. The smallest formation energy corresponding to configuration 1-2(2) is -1.74 eV (Table 1), this is the most optimal configuration among the studied configurations. Comparing the Ge-Ge bond length between the configurations we see that the Ge-Ge bond length in the 1-2(1) configuration is the largest (2.41 Å), and the Ge-Ge bond length in the configuration Figure 1-2(2) is the smallest (2.36 Å). The partial bond length shows the interaction

force between the atoms, the shorter the length, the stronger the bond between the atoms, so the maximum bonding force between neighboring Ge atoms is shown in the 1-2(2) configuration. Similarly, the bond length between Ge-B atoms in configurations 1-3(1) and 1-3(2) is the smallest (1.99 Å), and the largest is for configurations 1-2(1) (2.09 Å), it shows that the B-Ge bond is the most stable of the two configurations with the doping ratio B:Ge=1:3 (33.33%).

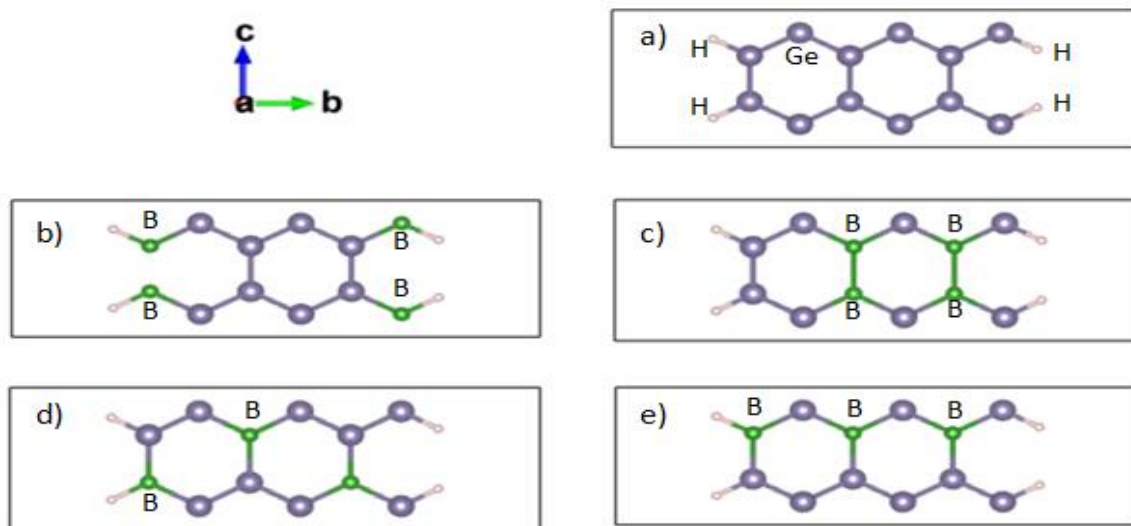


Figure 1. Unit cell of configurations: (a) Pristine; (b) 1-2(1); (c) 1-2(2); (d) 1-3(1); (e) 1-3(2)

The angle between two adjacent bonds indicates the structural flatness of the profiles. The data in Table 1 show that the angle α of the doping ratio B:Ge=1:3 is the largest (119.99°), which proves that these configurations are almost flat after doping B. When compared with pristine structure ($\alpha=109.32^\circ$), the angle α of all the doped configurations is larger than the alpha angle of the original configuration, so it can be concluded that when doping B the structures become flatter. The formation energy of the 1:2(2) configuration is the smallest (-1.74 eV), so it is the most stable configuration [25]. The energy of formation depends on many factors including the width of the nanoribbon and the atomic doping site. This formation energy is larger when comparing Pt, Ag, Au, Sn, In doping in GeNR with width 7 atoms and 8 atoms [27].

Table 1. Geometric structure and the formation energy

Configurations	Percentage	E_f (Formation energy (eV))	Ge-Ge(Å)	Ge-B(Å)	α (Degree)
Pristine	x	x	2.39	x	109.32
1:3(1)	25%	-1.35	2.38	1.99	119.99
1:3(2)	25%	-1.24	2.37	1.99	119.99
1:2(1)	33.33%	-1.45	2.41	2.09	111.93
1:2(2)	33.33%	-1.74	2.36	2.02	119.97

4. Electromagnetic properties

4.1. Energy band structure and multi-orbital hybridization

The bands of the pristine configuration do not cross the Fermi level (Figure 2a), indicating that this is a semiconductor with a narrow band gap (0.23 eV). The energy gap depends on the width of the nanoribbons. The band gap of the system is 0.48 eV and 0.02 eV with the width of the nanoribbons is 7 and 8 atoms, respectively [27]. The energy band structures and state densities of the doped configurations are shown in Figures 2c-f. Configuration 1-2(2) with a band

gap of 0.585 eV (Figure 2d) is a semiconductor; the remaining configurations are semi-metals with a small degree of state distribution around the Fermi level. The density of states is symmetric across the origin, so all configurations are antiferromagnetic structures with zero magnetization. With band gap extension to 0.585 eV. This band gap is greatly widened when comparing the doping In, Ag, Au, Sn, Pt in GeNRs with widths of 7 and 8 atoms [27], configuration 1-2(2) has great potential in room-temperature field-transistor applications. The above results show that the B-doped site is very important in the study of configurations, which not only change the properties of materials but also create suitable applications for each specific purpose. One possibility is that the foreign B atoms near the edge tend to form conductive structures, while the foreign B atoms farther away from the edge tend to form semiconductor structures. The contribution of the partial states Ge(s), Ge(p) was also investigated (Figure 1b), that of the s states is mainly in the deep energy region, while the contribution of the p-states is highly concentrated around the Fermi level.

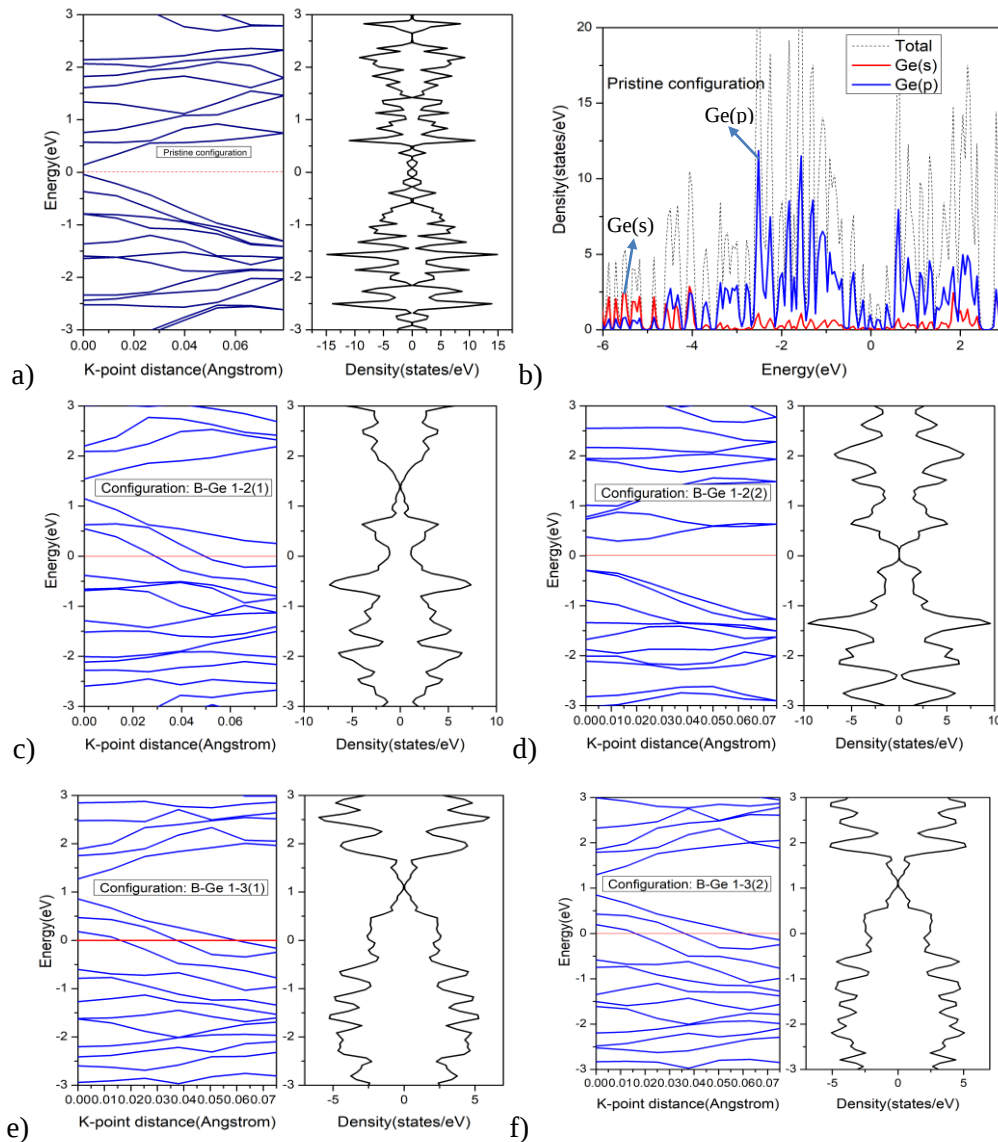


Figure 2. Band structure and density of states of configurations: (a) pristine; (c) 1-2(1); (d) 1-2(2); (e) 1-3(1); (f) 1-3(2). (b) Contribution of partial states of pristine configuration

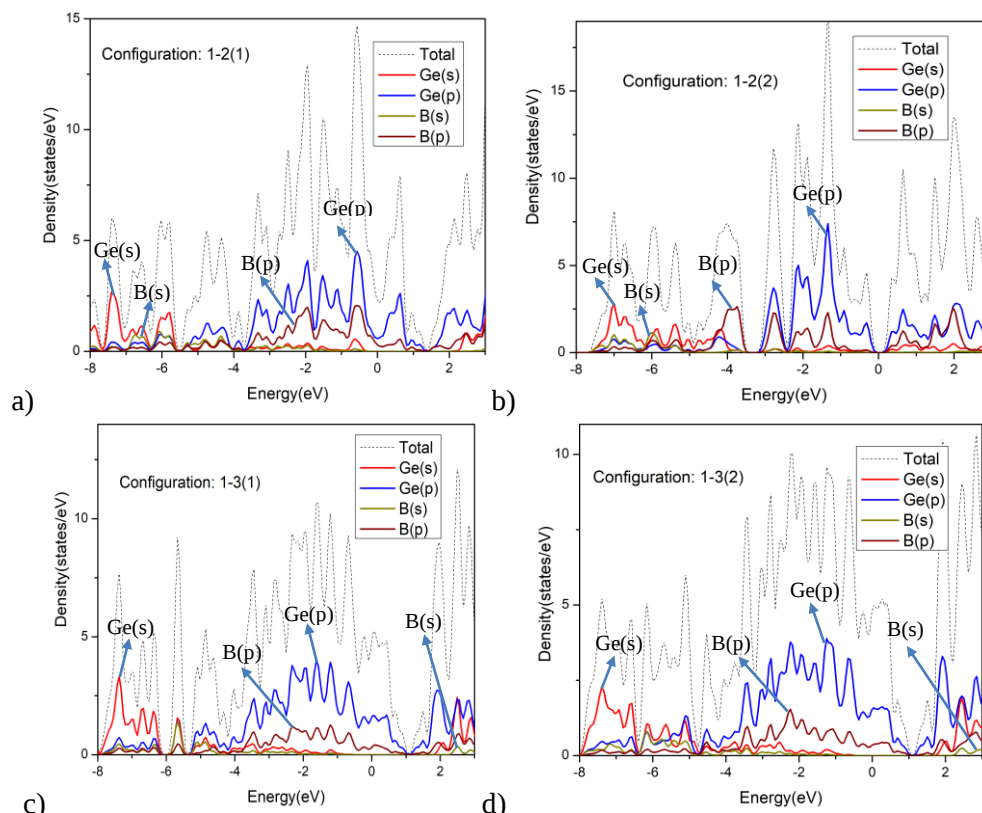


Figure 3. Partial states $Ge(s)$ (red line), $Ge(p)$ (blue line), $B(s)$ (dark yellow line), $B(p)$ (wine line) in the configurations: (a) 1-2(1); (b) 1-2(2); (c) 1-3(1); (d) 1-3(2)

Figure 3 represents the contributions of the partial states $Ge(s,p)$, $B(s,p)$ in the doped configurations and the s-p hybridization in the doped structures. The $B(2s, 2p_x, 2p_y, 2p_z)$, $Ge(4s, 4p_x, 4p_y, 4p_z)$ states overlap in neighboring electron clouds creating complex multi-orbital hybridizations. In Figure 3a, the hybridization between the $Ge(s)$ and $B(p)$ states is mainly concentrated in the energy region from -4 eV to -5.5 eV, while the hybridization of $B(s)$ and $Ge(p)$ is concentrated in the energy range from -5.5 eV to -8 eV. Similar to the other configurations (Figure 3b-d), the multi-orbital hybridization is mainly concentrated in the deep energy region from -4 eV to -8 eV, the reason here is that the deep energy regions are where strong σ bonds are created. In addition to the sigma bonds, which are the main force holding the B atom in the hexagonal lattice, there are weaker π bonds that also induce the formation of bonds between Ge and B. Doping density of B atoms also affects the extent orbitals overlap, the larger the density, the longer the overlap will spread on the energy axis. On the other hand, the fundamental difference in the contribution of partial states and multi-orbital hybridization between the configurations is also due to different doping sites, so the overlapping of orbitals at different energy levels is different.

The s-p hybridization is even more specific in Figure 4 (red dots represent $B(s)$ states, while blue dots represent $Ge(p)$ states). In the energy range from -4 eV to -10 eV, there is overlap between the red and blue dots, which represents the s-p hybridization in the bond between B and Ge. With a low doping ratio (Figure 4c,d), hybridization occurs in the deeper energy region (from -5.8 eV and beyond). This is quite consistent with the arguments above (Figure 3), which means that hybridization is more obvious when the density of doped B is large.

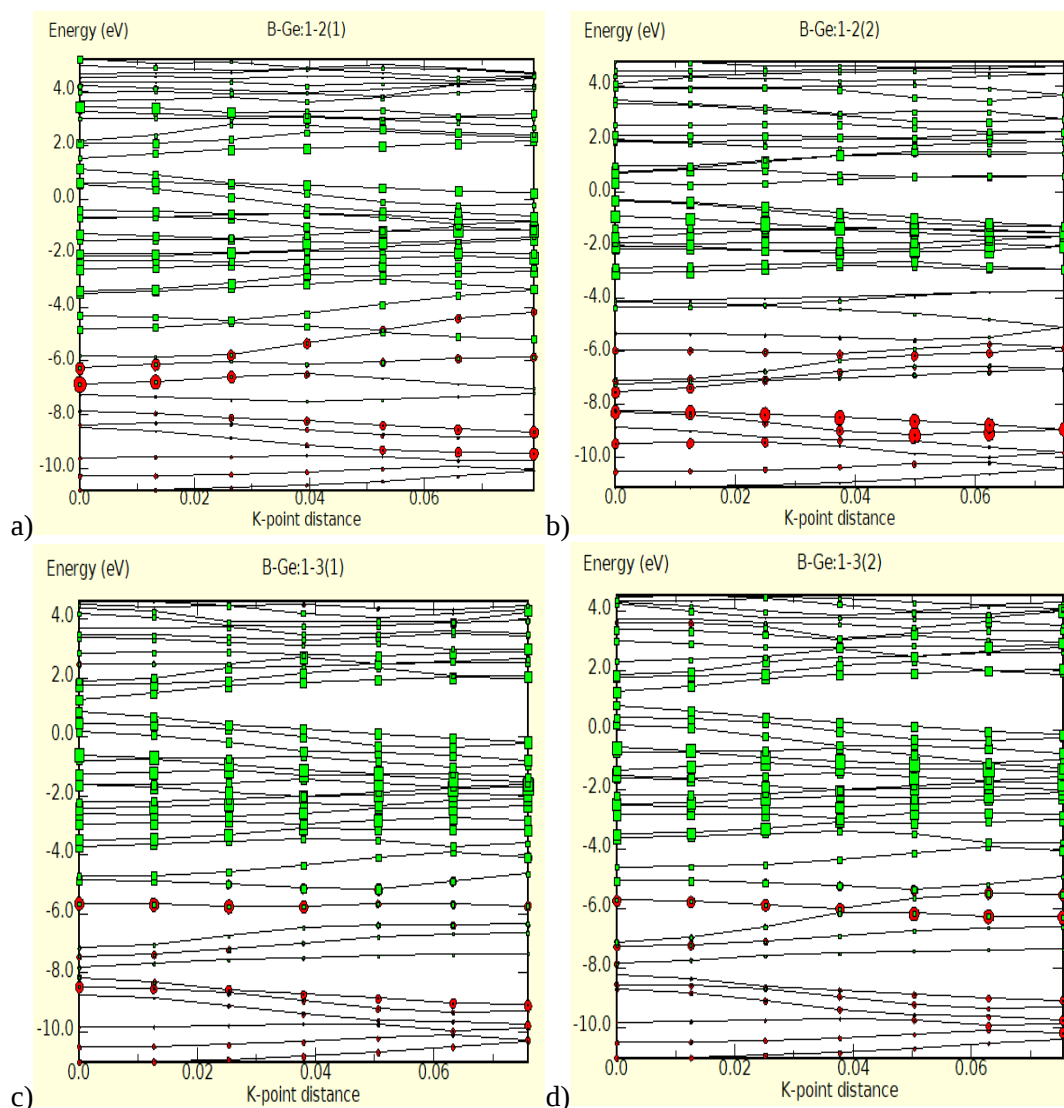


Figure 4. Hybridization $B(2s)-Ge(4p)$ in the configurations: (a) 1-2(1); (b) 1-2(2); (c) 1-3(1); (d) 1-3(2)

4.2. Charge distribution and charge density difference

In Figure 5, the red area is the place with a large concentration of electric charges, this region is also the representation of the sigma bond between atoms. The green region next to the red region on the line connecting the two atoms represents the pi bond between the atoms. The B-Ge bond shows more clearly and strongly than the Ge-Ge bond, this conclusion is completely consistent when studying the bond length in Table 1, the B atoms are kept very stable in the structure. hexagonal honeycomb bamboo. The B-B bond is the strongest of the bonds, it is shown in a red area that fills the space around the seam between them.

The charge difference indicates the amount of charge moving from one atom to another (Fig. 6: The yellow region is where the charge concentration is enriched, while the blue region is where the charges are lost (Fig. 6) empty hole)). When the B atoms are doped at the two edges (Fig. 6a), the charge displacement is concentrated mainly in B and H. With other configurations (Fig. 6b-d), there is an amount of charge displacement. From Ge to B, the space around B atoms concentrates a lot of charge, while holes appear around neighboring Ge atoms.

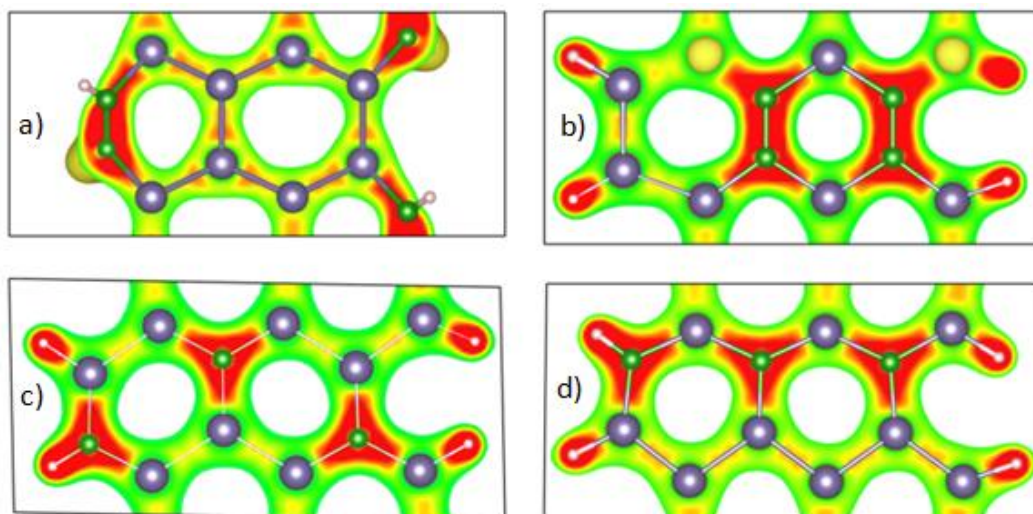


Figure 5. The charge distribution in the configurations: (a) 1-2(1); (b) 1-2(2); (c) 1-3(1); (d) 1-3(2)

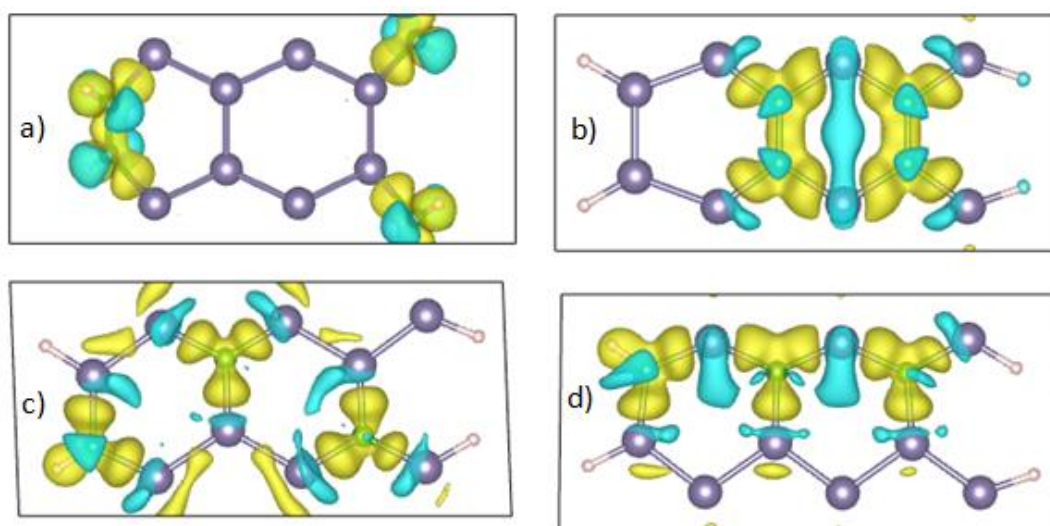


Figure 6. The charge density difference in the configurations: (a) 1-2(1); (b) 1-2(2); (c) 1-3(1); (d) 1-3(2)

5. Conclusions

This study focuses on two B doping ratios in GeNRs with four doping configurations. The doped systems are optimized after being optimized to keep the hexagonal honeycomb structure. The doping ratio B:Ge=1:3 shows that the post-doping structure is flatter, and the B-Ge bond is more stable. With the band gap opened up to 0.585 eV, the 1-2(2) doping configuration could be a potential application in field transistors. The s-p hybridization is very evident in the deep energy region from -4 eV to -10 eV. The charge distribution and difference were also studied, the B atoms gaining the charge, while the neighboring Ge atoms lost their charge. This research has the potential to create new materials that meet the increasing needs of science and technology.

Acknowledgement

This research is funded by Thu Dau Mot University under grant number DT.21.2.045.

This research used resources of the high-performance computer cluster (HPCC) at Thu Dau Mot University (TDMU), Binh Duong Province, Vietnam.

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