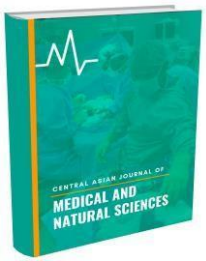

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Article

Enhanced h-BN Nanosheets Through Adsorption and Point Defects for Two-Dimensional Electronic Applications: A DFT Study

Zainab Shaker Mahmoud[1], Issa Z. Hassan[2]

1,2College of Education for Pure Sciences, University of Kirkuk, Kirkuk, Iraq
Correspondence: [1]ephm22009@uokirkuk.edu.iq, [2]ib.hassan@uokirkuk.edu.iq

Abstract: Hexagonal boron nitride (h-BN) is a leading two-dimensional (2D) material that features an atomic structure similar to graphene but is characterized by its wide band gap and exceptional insulating properties, positioning it as a promising option for nanoelectronics and dielectric applications. Nevertheless, its relatively large band gap of approximately 6 eV restricts its applicability in electronic devices that demand semiconducting characteristics. Consequently, this research aims to enhance the electronic properties of h-BN nanosheets by incorporating point defects and nickel (Ni) adsorption on the surface, employing Density Functional Theory (DFT) calculations under the GGA-PBE approximation, as implemented in the CASTEP code. Starting from pristine h-BN, we constructed defective structures containing boron and nitrogen vacancies, along with Ni adsorbed at various surface sites. The findings indicated that the introduction of point defects resulted in local structural deformations around the defect sites, leading to a complete loss of the band gap and a shift in electronic behavior from an insulating to a conducting state. On the other hand, the adsorption of Ni established a strong interaction between the Ni 3d and N 2p orbitals, resulting in a reduction of the band gap to 0.58 eV, which signifies a transition from insulating to semiconducting behavior. These results demonstrate that enhancing the electronic properties of h-BN nanosheets through the introduction of point defects and Ni adsorption is an effective approach, making them promising candidates for two-dimensional nanoelectronics and nanophotonic applications.

Keywords: Monolayer h-BN, DFT, Point Defects, Nickel Adsorption, Band Structure, Density of States, Electronic Properties

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1. Introduction

Two-dimensional (2D) materials are among the most remarkable discoveries in modern materials science due to their unique physical and electronic properties, which arise from their atomic thickness and high surface energy. The discovery of graphene in 2004 marked a turning point in this field, opening new horizons for developing novel monolayer materials with structural stability and promising potential for electronic and photonic applications [1]. Among these materials, hexagonal boron nitride (h-BN) stands out as one of the most chemically and thermally stable 2D materials. It possesses a graphene-like atomic structure composed of alternating boron and nitrogen atoms arranged in a hexagonal lattice connected by strong covalent bonds. The h-BN monolayer exhibits a wide band gap ranging from 5.5 to 6.0 eV, along with excellent structural and

chemical stability, making it an ideal dielectric substrate or insulating barrier for other 2D materials such as graphene and molybdenum disulfide (MoS_2). Its high oxidation resistance, thermal endurance, and atomically smooth surface make it a promising candidate for flexible electronics, 2D devices, multilayer nanostructures, and high-efficiency optoelectronic systems [2–4, 5]. The h-BN monolayer also demonstrates outstanding structural and stability, making it suitable for high-performance electronic and optoelectronic devices as well as multilayer nanostructures [6].

Despite these excellent characteristics, the wide band gap of h-BN limits its use in electronic applications that require semiconducting behavior. Therefore, researchers have focused on engineering its properties through both physical and chemical approaches, such as mechanical strain, point defects, atomic adsorption, and doping [4, 7, 8].

The properties of two-dimensional materials may be manipulated in various ways. Theoretical studies have demonstrated that the introduction of transition metal atoms, such as nickel (Ni), leads to strong hybridization between Ni orbitals and those of boron or nitrogen atoms, resulting in a reduced band gap and improved electronic performance [9]. Furthermore, adsorption processes can induce slight surface structural modifications that increase adsorption efficiency and stability, thereby expanding the potential applications of h-BN for advanced sensing and purification [9, 10]. Other studies have demonstrated that the electronic characteristics of two-dimensional materials can be adjusted through mechanical strain, which affects the lengths and angles of the B–N bonds within the lattice and, consequently, changes the band gap [11]. Alternatively, applying external electric fields can polarize the atoms in the layer, alter energy levels, and potentially trigger a transition from insulating to semiconducting properties [8, 12]. Research also shows that when point defects are introduced in h-BN, changes in structural flexibility and stability occur, and new electronic states emerge within the band gap [13, 14], indicating that these defects are a valuable method for adjusting electronic properties.

This study aims to investigate the effects of point defects and nickel adsorption on the structural and electronic properties of monolayer hexagonal boron nitride (h-BN). We will utilize density functional theory (DFT) calculations within the generalized gradient approximation (GGA-PBE). The goal is to understand the electronic mechanisms that influence band gap modification and to enhance the potential of this material for advanced two-dimensional electronic applications.

2. Materials and Methods

All calculations in this study were performed using Density Functional Theory (DFT) as implemented in the CASTEP module within the Materials Studio package .The Generalized Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was employed to accurately describe the exchange–correlation interactions among electrons. Optimized Norm-Conserving (OTFG) pseudopotentials were used to represent the electron–ion interactions, and the Koelling–Harmon relativistic treatment was included in all calculations. A (4×4×1) hexagonal boron nitride (h-BN) supercell consisting of 32 atoms was constructed, and a vacuum spacing of 15 Å was added along the z-axis to prevent interactions between adjacent layers. A plane-wave cutoff energy of 517 eV was employed to ensure the accuracy of the electronic calculations. The convergence parameters were defined as follows:

The total energy variation was less than 1×10^{-5} eV/atom, the maximum force on atoms was below 0.03 eV/Å, and the maximum atomic displacement did not exceed 0.001 Å. The geometry of the pristine h-BN nanosheet was first optimized to obtain its ground-state configuration. Subsequently, point defects were introduced by removing a single boron (V_B) or nitrogen (V_N) atom from the pristine structure, and all systems were fully relaxed until reaching the minimum total energy state. Afterward, adsorption calculations

were performed by placing a Ni atom on the surface of h-BN, allowing all atoms to move freely during geometry optimization to ensure the most stable configuration was obtained.

The adsorption energy (Eads) was calculated to evaluate the stability of the adsorbed system using the following expression:

$$E_{ads} = E_{h-BN+Ni} - E_{h-BN} - E_{Ni} \quad \text{..... (1)}$$

Where: $E_{h\text{-}BN+Ni}$ is the total energy of the system after Ni adsorption, $E_{h\text{-}BN}$ is the total energy of the pristine h-BN sheet, and E_{Ni} is the total energy of an isolated Ni atom.

3. Results and Discussions

3.1 Properties of Pristine Monolayer h-BN

The structural model of pristine hexagonal boron nitride (h-BN) was constructed using a 4×4×1 supercell consisting of 32 atoms arranged in an alternating sequence of boron (B) and nitrogen (N) atoms within a two-dimensional hexagonal lattice. The geometry optimization was performed within the framework of Density Functional Theory (DFT) using the Generalized Gradient Approximation (GGA–PBE) exchange–correlation functional, as implemented in the CASTEP code, until the system reached its minimum total energy. After relaxation, the h-BN sheets retained their planar hexagonal honeycomb structure with an internal bond angle of approximately 120°, a B–N bond length of 1.45 Å, and lattice constants of a = b = 2.51 Å, as illustrated in Figure 1.

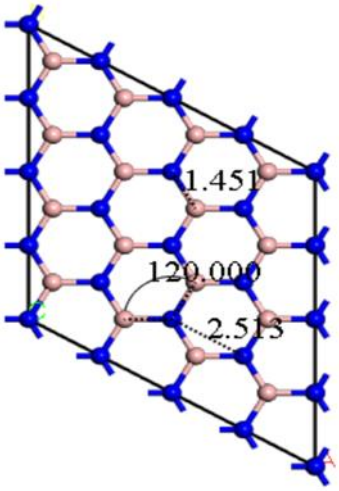


Figure 1. Geometrically optimized structure of a 4×4×1 supercell of pristine h-BN. (Color scheme: N, blue; B, brown).

These results show excellent agreement with previously reported theoretical values, confirming the reliability of the structural optimization and the accuracy of the adopted computational model. The band structure of the pristine h-BN monolayer shows a direct band gap of 4.66 eV located at the K point in the first Brillouin zone, as depicted in Figure 2a. The calculated band gap results for pristine h-BN, compared with previous studies, are presented in Table 1.

Furthermore, the total and partial density of states (TDOS and PDOS) analyses reveal that the valence band maximum (VBM) is primarily derived from N-2p orbitals. In contrast, the conduction band minimum (CBM) originates mainly from B-2p orbitals, as shown in Figure 2b.

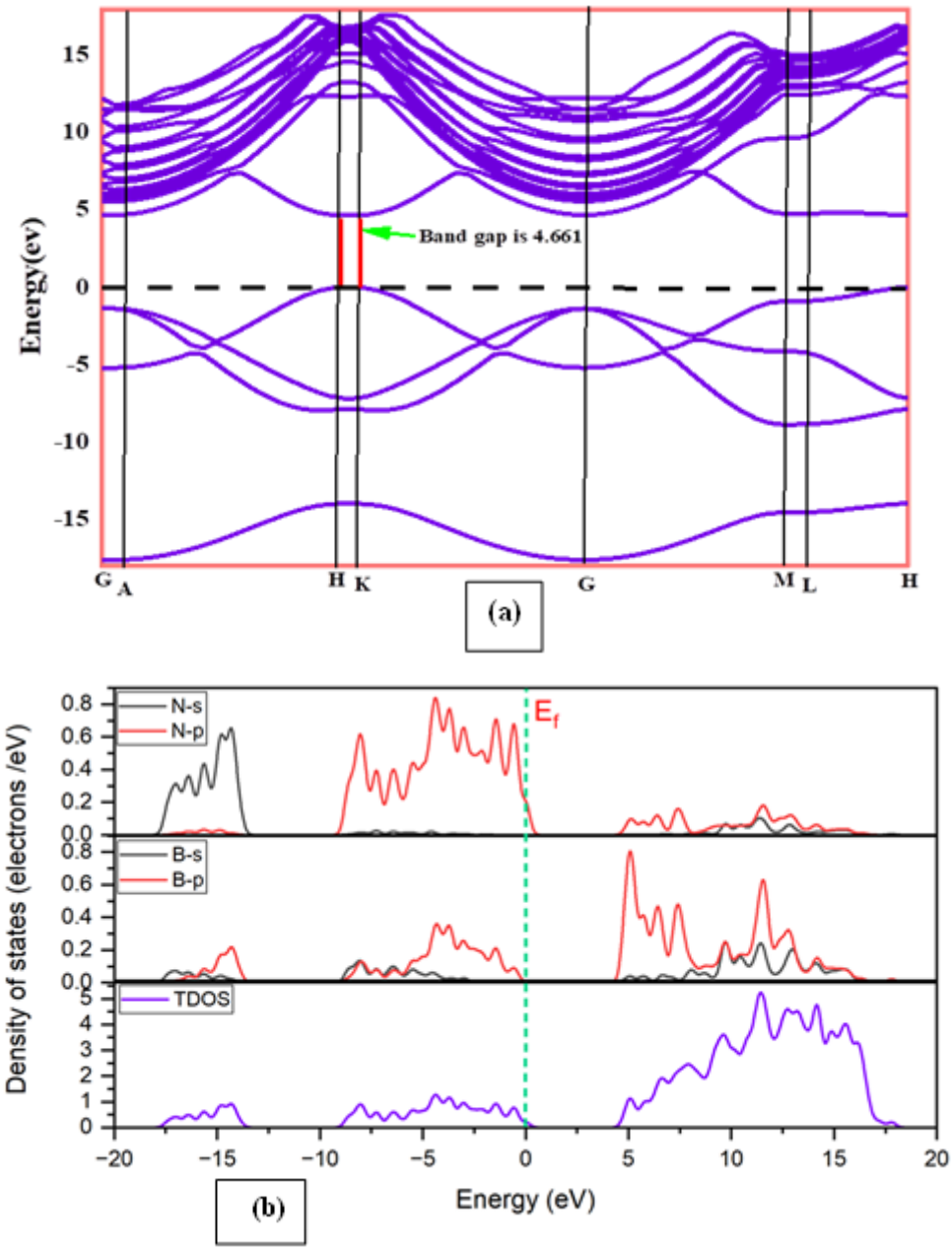


Figure 2. (a) Electronic band structure showing the direct band gap of pristine h-BN; and (b) Total and partial density of states (TDOS and PDOS) of pristine h-BN.

This electronic distribution indicates that the bonding between boron and nitrogen atoms is predominantly covalent, with a slight charge polarization toward nitrogen atoms, which explains the high structural stability and the wide band gap of h-BN. Therefore, the pristine h-BN monolayer can be considered a highly stable two-dimensional insulator, making it a promising candidate for use as a dielectric substrate or buffer layer in two-dimensional electronic and nano-optoelectronic devices.

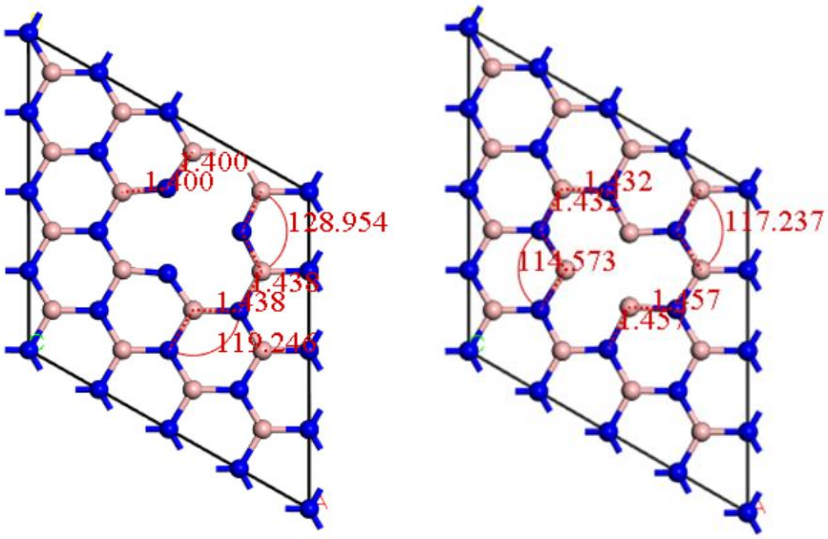
Table 1. Comparison of the calculated energy band gap of pristine h-BN with other reported results.

Band gap (eV)	Program	X-C correlation	Bond length (Å)	Reference
4.9	SIESTA code	GGA	1.45	[15]
4.55	SIESTA	GGA	1.45	[16]

4.661	CASTEP	GGA	1.451	Present work

3.2 Structural and Electronic Properties of Defected h-BN Monolayers (Vacancy Defects)

The influence of point defects on the structural and electronic properties of hexagonal boron nitride (h-BN) monolayers was investigated by introducing two types of atomic vacancies: nitrogen vacancy (VN) and boron vacancy (VB). Each defect was created by removing a single atom within a (4×4×1) supercell, and the structures were then fully relaxed to reach their lowest total energy configuration. The optimized geometries revealed that the formation of vacancies has a significant impact on the local bonding environment around the defect sites. In the case of a nitrogen vacancy (VN), the results showed a slight convergence of the surrounding boron atoms toward the defect site, where the average bond length was approximately 1.44 Å with an internal angle of about 116°, as illustrated in Figure 3a. On the other hand, for the boron vacancy (VB), a slight expansion of the neighboring bonds was observed, with an average bond length of about 1.42 Å and an internal angle of approximately 124°, as illustrated in Figure 3b.



(b) (a)

Figure 3. (a) Optimized structure of h-BN monolayer with nitrogen vacancy (VN); (b) Optimized structure of h-BN monolayer with boron vacancy (VB).

These structural variations suggest that the presence of point defects leads to local distortions in the hexagonal lattice, thereby affecting the overall structural stability of the h-BN sheet. From an electronic point of view, the band structures of both VN and VB systems reveal the appearance of new energy levels within the band gap, originating from the unpaired electrons surrounding the defect sites. The results indicated that the band gap completely disappeared in both cases, suggesting that the electronic behavior of the material transformed from an insulating to a conducting state, as illustrated in Figure 4. which is consistent with previous studies [17].

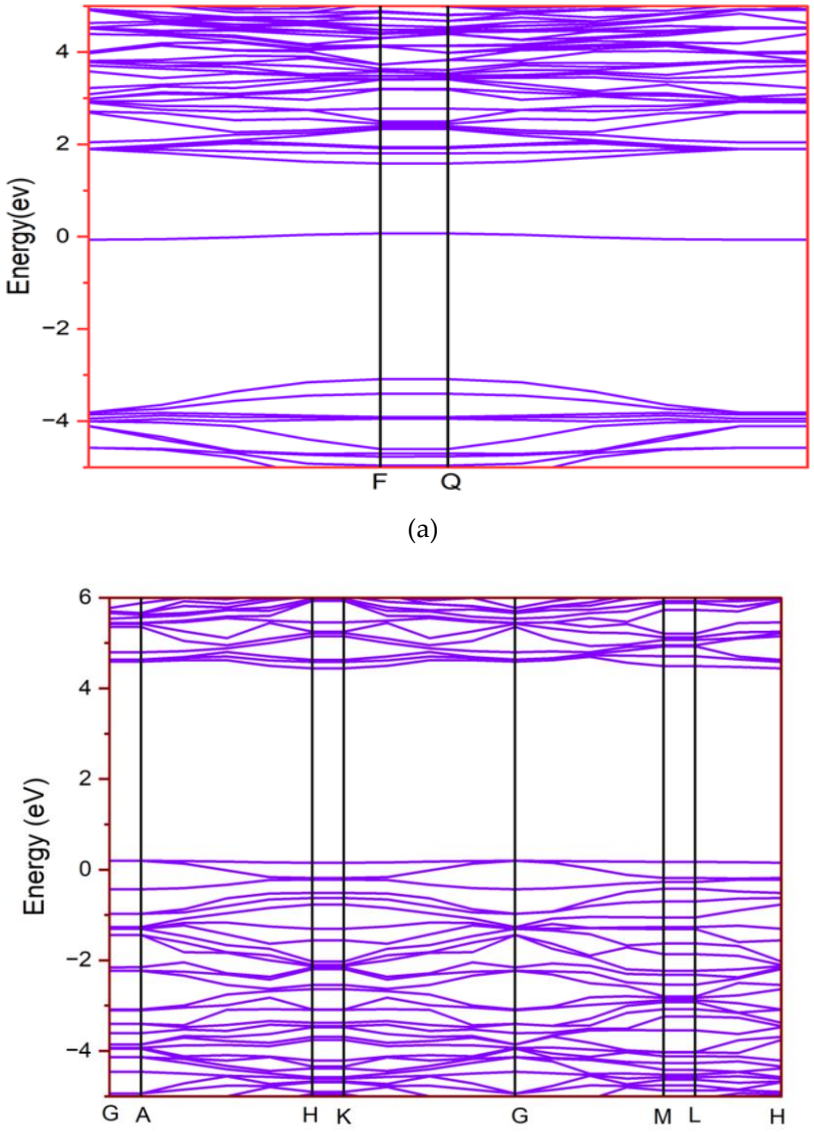


Figure 4. Electronic band structures of h-BN monolayer with (a) nitrogen vacancy (VN) and (b) boron vacancy (VB).

Analysis of the total and partial density of states (TDOS and PDOS) confirms that these newly formed states are primarily localized near the Fermi level, originating mainly from the B-2p and N-2p orbitals surrounding the defect sites, as shown in Figure 5. These findings demonstrate that introducing vacancy defects into h-BN monolayers causes a redistribution of electronic density near the Fermi level, enabling the practical tuning of electronic properties through controlled defect engineering.

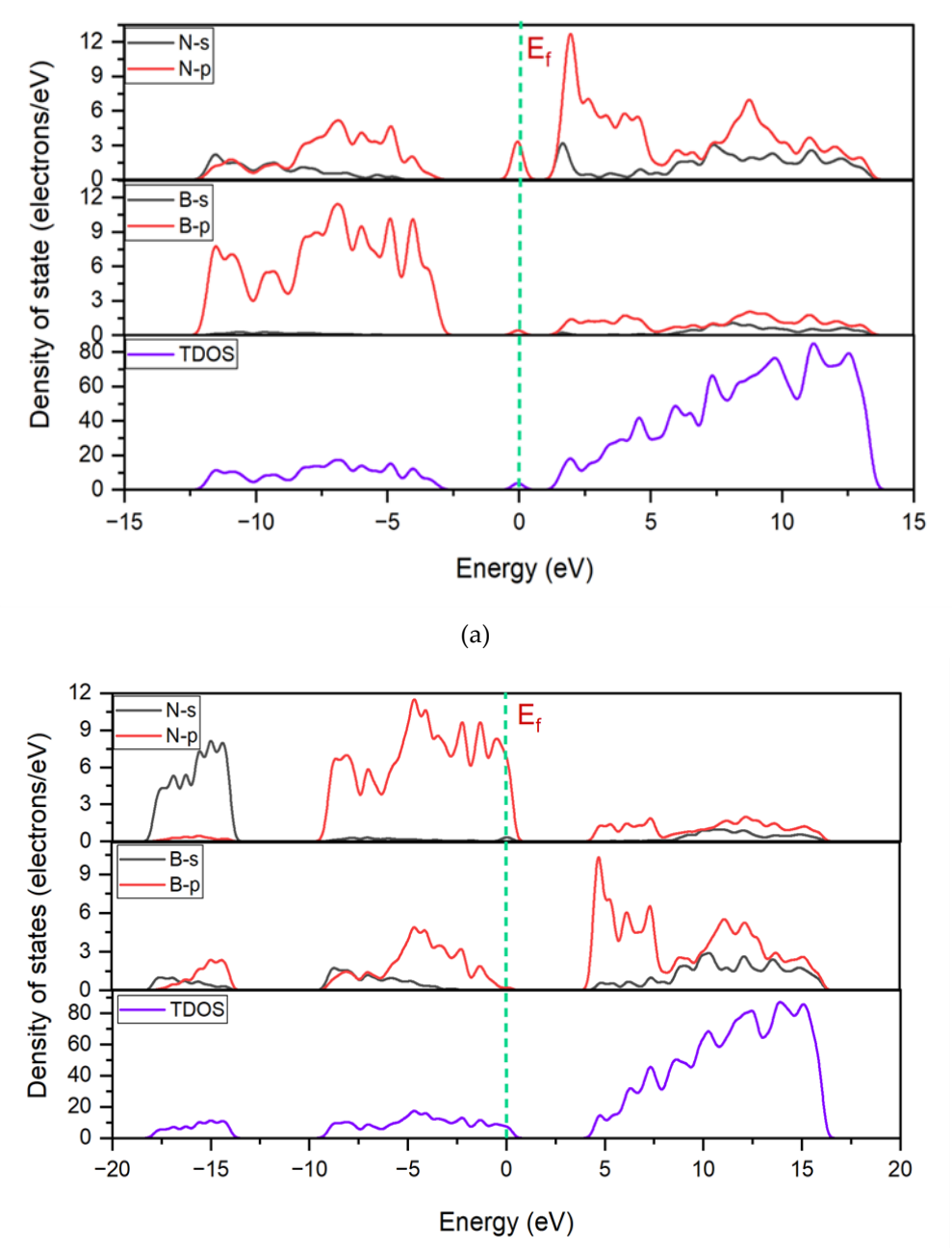


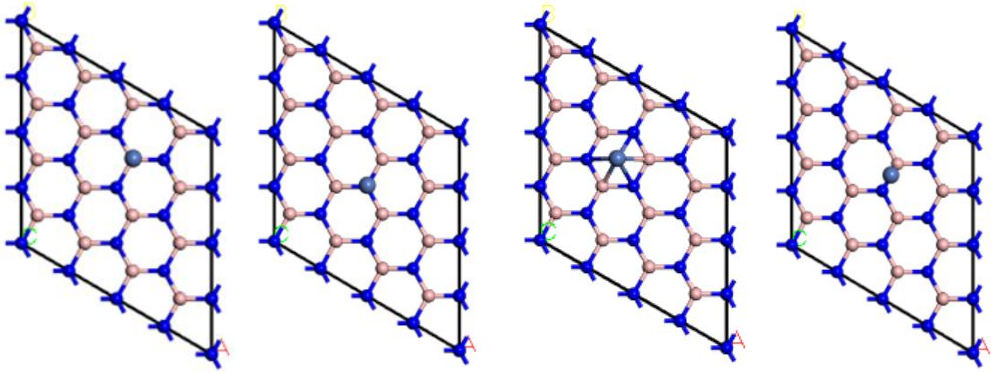
Figure 5. Total and partial density of states (TDOS and PDOS) of h-BN monolayer with (a) nitrogen vacancy (VN) and (b) boron vacancy (VB).

3.3 Properties of Ni Adsorption on Hexagonal Boron Nitride Monolayer

The adsorption of a nickel (Ni) atom on the surface of the hexagonal boron nitride (h-BN) monolayer was investigated by considering four possible adsorption sites, as follows:

(a) above the boron atom, (b) above the nitrogen atom, (c) at the center of the hexagonal ring, and (d) above the midpoint of the B–N bond, as illustrated in Figure 6. After performing geometrical optimizations for all configurations, it was found that the most stable site is position (b), i.e., above the nitrogen atom, where the lowest adsorption energy of −13.61 eV was obtained. The negative value of the adsorption energy indicates that the process is exothermic and occurs spontaneously, confirming the thermodynamic stability of the Ni-adsorbed h-BN system.

This stability arises from the strong interaction between the Ni and neighboring N orbitals at the adsorption site.



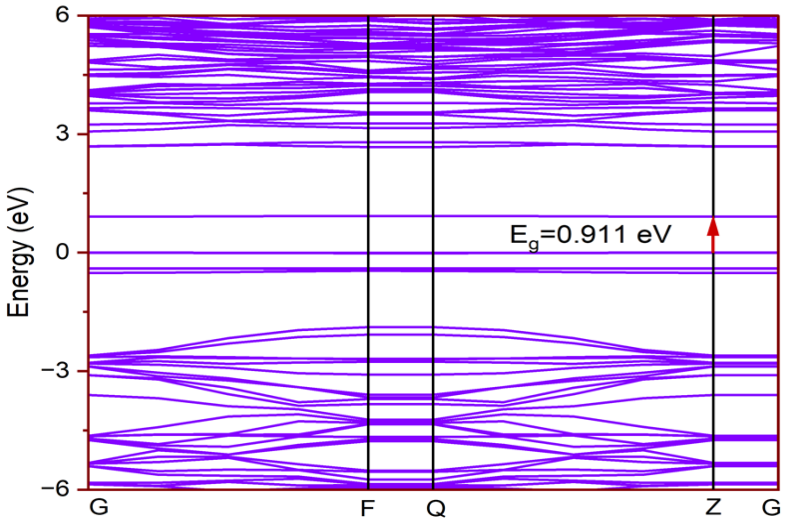
(a) (b) (c) (d)

Figure 6. The possible adsorption sites of the Ni atom on the h-BN surface: (a) above the boron atom, (b) above the nitrogen atom (the most stable site), (c) above the center of the hexagonal ring, and (d) above the B–N bond.

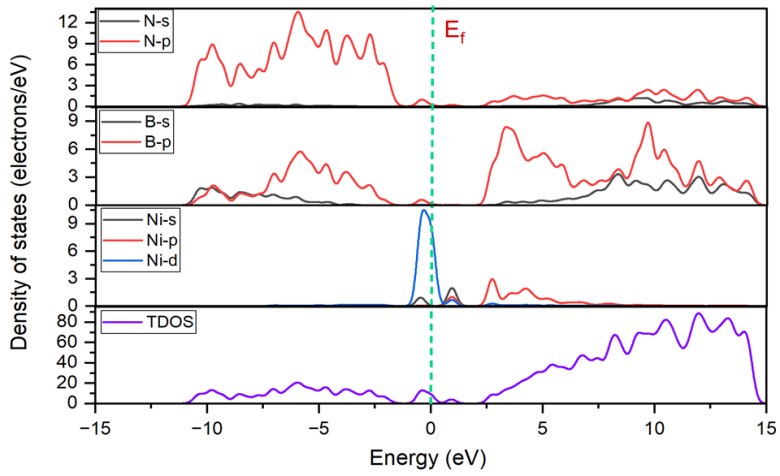
A slight change in the bond lengths surrounding the adsorbed Ni atom was observed due to electronic interactions, while the overall hexagonal structure remained stable without significant distortion. The average bond length between the Ni and N atoms was measured to be roughly 1.85 Å, suggesting a relatively strong bonding interaction between the Ni adatom and the h-BN surface. From an electronic perspective, the analysis of the band structure indicated that the band gap of the Ni-adsorbed system reduced to approximately 0.58 eV, which is considerably less than that of the pristine h-BN monolayer, signaling that Ni adsorption causes a shift in the electronic characteristics of the material from an insulator to a semiconductor, as illustrated in Figure 7a.

Furthermore, the total and partial density of states (TDOS and PDOS) plots, illustrated in Figure 7b. demonstrated a clear contribution of the Ni-3d and N-2p orbitals near the Fermi level, confirming a strong orbital hybridization between Ni and the surface nitrogen atoms. This hybridization leads to a redistribution of the electronic density within the band gap, explaining the observed reduction in its value. This behavior is consistent with previous studies, which reported that the adsorption of transition-metal atoms on the h-BN surface induces new electronic states near the Fermi level and leads to a noticeable reduction in the band gap due to the strong hybridization between the adsorbed atom and the surface atoms [18].

Overall, these results suggest that Ni adsorption is an effective strategy for tuning the electronic properties of h-BN nanosheets, thereby enhancing their potential for applications in nanoelectronics and two-dimensional sensor devices.



(a)



(b)

Figure 7. (a) Band structure of Ni-adsorbed monolayer h-BN. (b) Total and partial density of states (TDOS and PDOS) of Ni-adsorbed monolayer h-BN.

4. Conclusions

This study investigated the structural and electronic properties of monolayer hexagonal boron nitride (h-BN) nanosheets using Density Functional Theory (DFT) calculations within the Generalized Gradient Approximation (GGA-PBE). Three systems were examined: pristine h-BN, h-BN with defects, and Ni-adsorbed h-BN. The findings revealed that the pristine h-BN structure exhibits high structural stability, characterized by a wide band gap of approximately 4.66 eV, which confirms its insulating nature and electronic stability. In contrast, the introduction of point defects, specifically boron and nitrogen vacancies, caused local distortions around the defect sites and generated new electronic states near the Fermi level. This led to a complete disappearance of the band gap, resulting in a transition of the material's electronic behavior from an insulator to a conductor. The study on the adsorption process revealed that the most stable adsorption site for the nickel (Ni) atom is situated above the nitrogen (N) atom, with an adsorption energy of -13.61 eV. This negative value indicates that the adsorption process is spontaneous and thermodynamically stable. Additionally, electronic analysis revealed a reduction in the band gap to 0.58 eV, which is attributed to the strong hybridization between the Ni-3d and Ni-2p orbitals. This hybridization altered the electronic properties, resulting in the behavior of h-BN shifting from insulating to semiconducting material.

In summary, both the introduction of point defects and the adsorption of Ni have proven to be effective approaches for tuning the electronic properties of monolayer h-BN, thereby enhancing its potential for applications in advanced nanoelectronics devices and two-dimensional sensors.

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