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Effect of metal ad-atoms on the structural, electrical, and optical properties of boron-nitride nanostructures towards optoelectronics: a DFT based study

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Abstract

In the present study, we investigate the structural, electronic, and optical properties of pure and doped boron-nitride (BN) nano-systems using density functional theory (DFT) simulations. Metal dopant C, Ni and Cu were introduced. Structural properties, such as bond length and formation energy, were observed, and the bond lengths were found to agree with experimental results previously reported in the literature. The metal atoms in the metal-doped BN nanosystem were shown to have a direct effect on the nature of the surface. The calculated formation energies show that the stability of the BN nanosystem is enhanced upon metallic doping, as clearly shown in the case of Ni-doped boron nitride (NiBN). The metal dopant is found to reduce the energy gap and enhance overall electrical conductivity. UV-Visible spectrum calculations show that the metal atom causes a red-shift in the spectrum towards the red wavelengths. Open-circuit voltage (VOC) calculation shows that Ni-doping of BN enhances the VOC by 420 meV with respect to pristine BN, thereby confirming the positive impact of the dopant Ni on the two-dimensional h-BN surface and consequent possible usefulness in optoelectronics.

Keywords: DFT, Boron-Nitride, Open Voltaic Circuit, Molecular Orbitals, UV-Visible

1. Introduction

Boron-nitride (BN) is an inorganic equivalent of graphite. It has allotropes like nanotube, nanowire, nanoribbon, nanocone and nanorod[1]. BN nanoribbon has been already synthesized a few months after the discovery of graphene in 2004[2]; and over the past two decades, these allotropes and hybrids have attracted significant attention thanks to their wide applications in optics, optoelectronics, spintronics, and as electric insulators[3]. BN has been found to form a crystal structure similar to that of graphene, consisting of an equal number of nitrogen and boron atoms. in a honeycomb structure. The atoms of the BN nanosheet form sp^2 bonds in a two-dimensional layer[4]. Pristine BN has a wide bandgap of approximately 5.9 eV[4, 5]. Because of its excellent electrical insulator property, it has been found applications as a charge leakage barrier layer in electronic equipments[7]. It also shows far-ultraviolet light emission, which can possibly be attributed to its wide direct band gap[8]. It is well known that nanostructures, such as nanotubes, nanoribbons have unique properties that depend on their size and curvatures [8, 10]. BN monolayer nanoribbons have unique chemical and electric properties, and promise a wide range of applications, such as protective coating, deep UV emitter, and translucent membranes of BN materials[9]. Many researchers have utilized doping

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mechanisms to modify the structural, electronic, and optical properties of BN nanoribbons. As an example, in report[11] Mohammed *et al.* reported a decrease of the band gap of a BN nanosystem from 5.9 to 3.1 eV, changing its electronic behavior from insulator to semiconductor. Doping has also been reported to enhance the electrical conductivity[12, 13]. The aim of this work is related to this: studying the effect of doping processes on BN nanostructures. In this work, we consider carbon, nickel, and copper atoms as dopants. Our aim is to **investigate the effect of metallic doping on the electronic, structural, and optical properties of boron-nitride nanomaterial, and its application perspective in optoelectronic devices.**

2. Simulation tools

In the present study, nanotube modular software was used to generate a BN nanoribbon structure, which was visualized via the Gaussian View 5.0 software. The electronic, structural, and optical properties of the pure and the doped systems were computed using Gauss View 5.0 V and Gaussian 09 W .The studied structural properties involved bond lengths, angles between atoms, and binding energy; the electronic properties involved molecular orbital energy, band gap, ionization potential, and electron affinity; and the optical properties involved the UV and visible spectrum, the determination of the maximum wavelength of absorption and the types of shifting[14]. All results were obtained via density functional theory (DFT) simulations using B3LYP hybrid functional and the Las Alamos National Laboratory 2 Double-Zeta (LAN2DZ) basis set [15].

3. Geometrical properties of pure and doped system.

In this section, we study the effect of copper (Cu), nickel (Ni) and carbon (C) atoms on the structural properties of BN, such as bond lengths and the binding energy. The structures of pure and doped boron-nitride systems after geometrical relaxation are shown on Figure 1. The bond length between B-N, B-H and N-H atoms in the relaxed systems were 1.4233-1.4655 Å, 1.1880-1.1992 Å, and 1.0121-1.0142 Å respectively. All bond lengths in present study were in agreement with previous reports [13, 9]. The doping of boron nitride by metal atom also changes the planar structure and the bonds between atoms. In case of the Cu dopant, we can notice some stretching in the structure between the Cu atom and the three neighboring atoms. A similar effect is also present in case of Ni dopant. We can also notice that the Ni atom causes a clear stretching in the structure, and appears as a raised defect. The carbon dopant doesn't show any significant effect on the relaxed structure of BN, and remains in planer shape, similarly as reported in [17]. An important cause of the stretching that appear in the BN system when doped by Ni and Cu atom is the higher atomic number of the dopants than that of the boron and nitrogen forming the BN system[18].

Table 1 shows the average bond length and the binding energy (E_b) of the doped systems, which can be calculated as follows

$$E_b\ (eV) = [E_{MBNNR} - (15*E_N + 15*E_B + 15*E_H + 1*E_X)]/N, \quad 1$$

where E_{MBNNR}, E_N, E_B, E_H, E_X and N are the total energy of the doped BN nanoribbon, nitrogen, boron, hydrogen and doped metals atoms and numbers of atoms respectively. The binding energy of the systems is decreasing as BNNi > BNCu > BNC, showing that the Ni-doped BN is more stable than the other studied systems, and the Cu-doped system is more stable than the C-doped one. These results indicate that BN can be doped by metallic atoms[22].

Table 1: average bond length and binding energy of the studied nanosystems computed by DFT method using the LAN2DZ basis set.

System	bond length in the present study (Å)	Average bond length in the previous study (Å)	Binding energy (eV)
BN-Cu	**1.7731**	**1.7500-1.9100**[19]	**-11.8345**
BN-Ni	**1.7879**	**1.6800-1.8100**[20]	**-15.1135**
BN-C	**1.3680**	**1.3500-1.3800**[21]	**-5.6053**

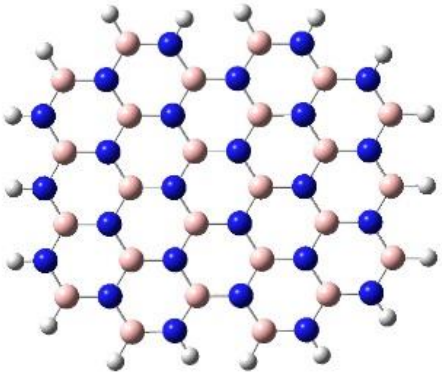
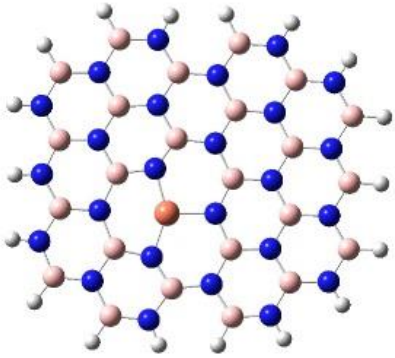
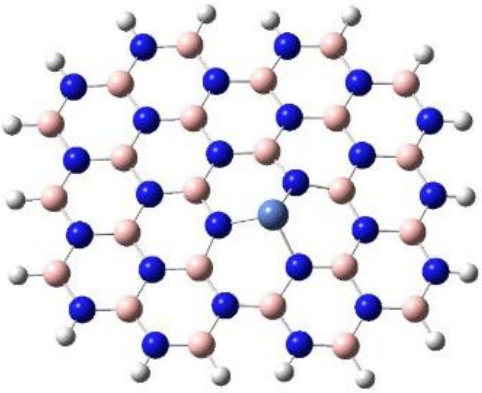
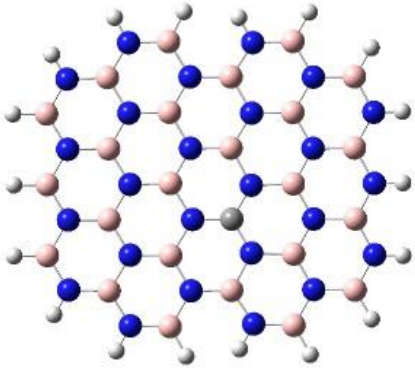
Systems	Structures
BN	
BN-Cu	
BN-NI	
BN-C	

Figure 1: representative geometrical structure of the pure and doped BN nanosystems.

Energy gap and molecular orbitals of pure and doped BN nanomaterials.

The energy band gap is considered to be one of the important factors that determine the nature of materials (conductors, semi-conductors and insulators) depending on change in molecular orbitals energy[23]. The variation of the energy gap (HOMO-LUMO) for the studied pure and doped BN nanomaterials are plotted on figure 2. This variation follows the following trend: BN > BN-C > BN-Cu > BN-Ni. We can notice that pure boron nitride in pure state is an insulator with a bandgap of 6.261 eV, in agreement with a past study in [24]. It can be observed that the bandgap of the doped BN systems drastically decreases from 6.261 to 1.433 eV, which can be attributed to the ease of electron transfer between HOMO and LUMO, favoring high conductivities for metal doped BN nano-materials[25]. In general, our results show that the presence of the metal atom decreased the band gap from that of an insulator to that of a semiconductor material, proving that such doping can be considered as an important tool to modify the electronic properties[26].

Table 2 lists the energy of the HOMO and LUMO orbitals and the band gap of the pure and doped BN nanosystems in eV unit. Our results show that the presence of dopants has a direct effect on molecular orbitals energy, shifting them to lower energies. This is clearly shown in the HOMO of the Ni- and C- doped systems. The HOMO energy of the Cu-doped system becomes unstable because it is shifted to a high energy level[27]. Our results also show that that all LUMO levels were shifted to lower energy ranges[28]. The HOMO and LUMO molecular orbitals of the studied nanosystems are shown on Figure 3. For the pure BN nanosystem, our results show that the HOMO and LUMO are mainly localized on the B and N atoms respectively. This is in agreement with the electron-rich and electron-deficient characteristics of nitrogen and boron atoms. In the doped case, the distribution of molecular orbitals is changed because of the addition of the metal atoms to the nanosystems[29]. Our results show that all LUMO charge density is distributed around the dopant atoms, on the other hand, a high concentration of valance electrons was formed[19]. The results also indicate that most of the HOMO charge density is located at the edges of the doped BN nanosystem[30].

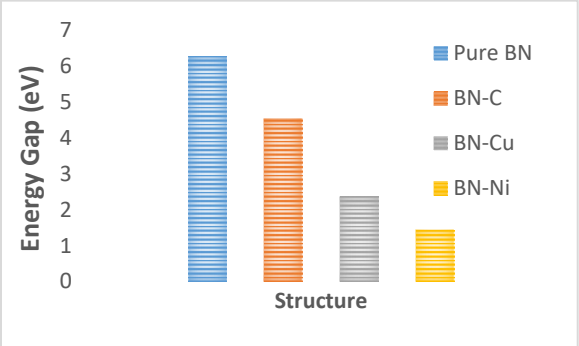


Figure 2: representative variation of the energy gap for pure and doped BN nanomaterials computed by DFT method using LAN2DZ basis set.

Table 2: Calculated HOMO and LUMO energy and energy gap of the pure and doped BN nano-systems measured in eV.

Systems	HOMO	LUMO	Energy Gap
BN	-6.6740	-0.4133	6.261
C-BN	-9.4482	-4.9053	4.542
Cu-BN	-6.6177	-4.2582	2.359
Ni-BN	-9.4019	-7.9687	1.433

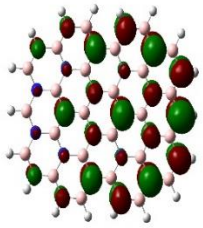
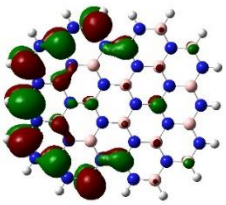
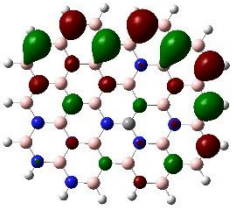
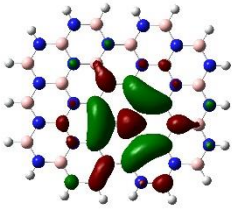
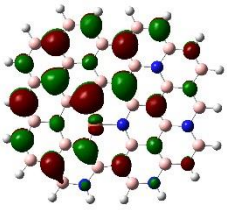
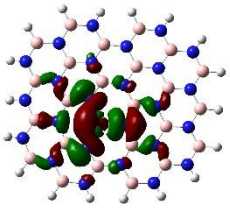
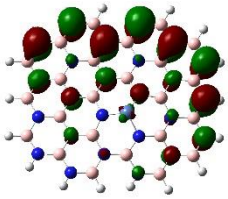
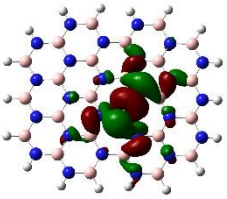
S.	HOMO	LUMO
BN		
C-BN		
Cu-BN		
Ni-BN		

Figure 3: representative distributions of the molecular orbital charge density and the type of bonding is σ, σ*, π, and π* [GN:? DON'T SEE THE ORBITAL TYPES…].

1 UV-Visible spectrum

TDDFT calculations were performed on the ground-state optimized structures using the LAN2DZ basis set and the B3LYP hybrid functional. Table 4 lists the values of the optical band gaps and the maximum wavelengths of absorption of the nanosystems under study. The purpose of the investigation of the optical band gap is to determine the energy of transition. The optical band gap energies were found to be in the range 6.2-0.9 eV, which indicate the ease of the optical absorption in the case of doped systems. The difficulty in optical absorption was clear in case of the pure BN nanosystem, which has a wide optical band gap of 6.2 eV[31]. The optical absorption seems to be more favored in the case of metal doped BN nano systems (having smaller optical band gap), which could be availability of more intermediate energy states due to the doping[32]. The UV-Visible absorption spectrum of pure and doped BN nanosystems computed by TDDFT is shown on Figure 4. The results show that doping the BN nanosystem by metal atom causes a shift in the spectrum towards the red side[33]

Table 4: Calculated values of the optical band gaps and maximum wavelengths of absorption of the studied nanosystems.

System	Maximum wavelength of absorption (λ_{max}) (nm)	Optical band gap (eV)
Pure BN	200	6.2
BN-C	300	4.133
BN-Cu	750	1.653
BN-Ni	1350	0.918

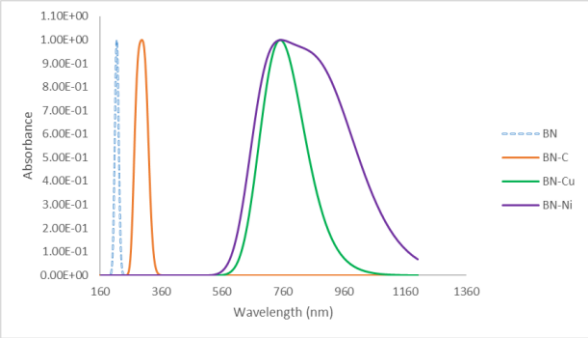


Figure 4: The UV-Visible spectrum of pure and doped BN nano systems computed by TD-DFT at basis set LAN2DZ with hybrid function B3LYP

Open-circuit voltages

The open-circuit voltage (VOC) is considered to be an important property that pointed gain voltaic for proposed nano-system. The VOC can be calculated as shown in Eq. 2, and it describes the difference between the LUMO of the nanosystem and the conductive band minimum of TiO_2 ($CBM_{(TiO2)}$)[34].

$$VOC = Abs\ (LUMO_{(nano\text{-}system)} - CBM_{(TiO2)}) \quad 2$$

Before the addition of the metal atom, the VOC of the BN nanosystem is 3.58 V. The results show that the BN nanosystem have high gain voltaic. In the second part, we add metal atoms to the BN skeleton, and investigate their effect on the voltaic properties for the studied nanosystems. The VOC calculated using Eq. 3. is presented in Table 5. The results show that the metal atoms have a direct effect on the VOC. We can observe that the nanosystems doped with Cu and C atoms have a decreased VOC of 0.90 and 0.25 V. Oppositely, the Ni atom causes an increase of the VOC from 3.58 to 4 V. Altogether, the VOC of the pure and doped systems follow the order of BNNi>BN>BNC>BNCu. These results show Ni to be the favorable dopant for applications in photovoltaic devices.

Table 5: VOC of the investigated systems.

Systems	V_{OC} (Volt)
BN	**3.58**
C-BN	**0.90**
Cu-BN	**0.25**
Ni-BN	**4.00**

Conclusions

- Metallic doping of BN nanosystem enhances its electronic properties such as the energy gap.
- The doping causes, the energy gap of BN to decrease from 6 to 0.9 eV, and enhances electrical conductivity.
- The optical absorption spectra shift towards the red region of the electromagnetic spectrum. As well as electrons needed small amount of energy for transition from HOMO to LUMO and this clear in Cu-BN system
- The calculated formation energy shows the feasibility of doping BN by metal atoms.

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