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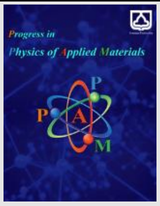

Different behavior of Nano sheet and Bulk of the hexagonal boron nitride with first principal calculation approach

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ABSTRACT

In the present work, the electronic, optical, and nano structural properties of boron nitride samples (in monolayer, bilayer and bulk form) were determined with the help of density functional theory (DFT) and calculations using the Siesta package and the generalized gradient approximation (GGA). -PBE) has been discussed. It is found that the bond length, bond angles, and curvature values of boron nitride are almost the same in monolayer, bilayer, and bulk states. Of course, these structures are considered to have planar forms. Considering the existence of the low band gap energy between the bottom of the conduction band and the maximum of the valence band, (although the size of the bandgap decreases with the increase in the number of layers), it can be concluded that the samples are semiconductors.

Since there is a relationship between refractive index, magnetic permeability, and electrical permeability (magnetic parameters are not discussed in the present work), dielectric function, reflection coefficient, absorption coefficient, and refractive index are also investigated. The two real and imaginary components of the dielectric function are important in the properties of materials in terms of nanocomposites. Here, special attention is paid to the main peak in the real part of the dielectric constant.

1. Introduction

Boron nitride with chemical formula BN, has high thermal and chemical stability and can only be synthesized in the Labs (so it cannot be found in nature.). Its good advantage can be attributed to having different structures such as zinc blend, hexagonal, and wurtzite. Hexagonal shape (it is rare and, in its graphite form, is very stable and of course it is soft among polymorphs of BN), cubic type (c-BN after h-BN) has stable structure. It appears in the forms of g-BN and h-BN, α-BN and some other parameters such as inter-band transitions need to be considered [1-7]. These material as Boron nitride ceramics can be used in high-temperature equipment due to their excellent thermal and chemical stability and in nanotechnology chips [5,6].

Boron nitride is also considered to have a hexagonal structure similar to graphite, in each layer the boron and nitrogen atoms are connected by strong covalent bonds, while the layers themselves are connected by weak van der Waals bonds. In other words, they exhibit an SP^2 hybridization. However, the pattern between the layers of these planes differs from the observed pattern recorded for graphite, as the boron atoms located on and above the nitrogen atoms hide these atoms from sight.

In the case of nanometer-scale materials, it has been reported that it has an aspect ratio less than 1. The density functional theoretical calculations based on the ab-initio effect can be used to investigate uniaxial and biaxial tensile and compressive strains on the performance of h-BN and boron carbon nitride (BCN) monolayers. The fact that unlike h -BN, which has a band gap of 5 eV, the calculated direct band gap transition of BCN monolayer is 1.18 eV indicates that BCN is useful for optoelectronic applications [8].

DFT calculations on h-BN monolayers, compared to carbon substitution impurities (CB, CN), demonstrated that

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both boron and nitrogen vacancies (VB, VN), and other types of vacancies, especially Stone-Wales defects (SW) play the role something like carrier traps and can therefore influence to localized modes in the ban gap energy. It means that BN in h- BN structure can behave like semi- metallic samples and also be suitable for rapid screening of faulty systems [9].

Some people [8-11] have tried to study and investigate the possible applications of different BN structures with different electronic and optical characteristics for many kinds of chips such as hydrogen storage systems (with Ni dopant crystallites), photocatalytic devices (confirmed with using First-principles calculation- DFT, Fuel cells (In this regard: h-BN sheet with reduced graphene oxide (RGO) or reduced graphene fluoride (RGF) has been used), and optoelectronic devices.

Beside them, in the present work, we study the effect of changing the number of layers on the structural, electronic, and optical properties of boron nitride to see if these different structures can be used for optoelectronic devices in future.

2. Computational Methods

In the present work, all the calculations were done using the SIESTA package [12] and based on the density functional theory (DFT). The generalized gradient approximation (GGA) introduced by Perdew-Burke and Ernzerhof (PBE) has been used for exchange-correlation functional [13].

Since it is clear that some key parameters such as the number of k points and the convergence factor as well as the correlation coefficient are very important in the accuracy and speed of the calculations, the calculations were performed in a self-consistent manner, and in that the appropriate cut-off energy equal to 160 Ry has been found for separating the core states from the valence states for all bulk, monolayer (single-layer), and bilayer (two- layer) structures, and finally the minimum of total energy of the system is determined. The number of k points in the Monkhorst-pack grid was chosen as (8×8×8) for the bulk structure and (8×8×1) for the monolayer and bilayer structures. It is worth noting that the exchange (direct and indirect) interaction, dipole- dipole interactions, and the interactions between the adjacent layers in the monolayer and bilayer, were not considered due to substituted process of B(N) on C(N) states. There is, in fact, a sufficiently large number of unoccupied states, in that it is necessary to consider the direction perpendicular to the boron nitride sheet (Z direction) and for bulk and bilayer structures, the distance between the layers be about 3 Å. Also, the optimized lattice constants after the relaxation stage of the system, for the boron nitride structures of monolayer, bilayer, and bulk were;

$a = 2.58$ Å, $b_x = 1.2$Å, $b_y = 2.2$ Å

Therefore; by applying these parameters, the system is completely relaxed so that the force on each atom is less than 0.01 eV/Å.

To study the optical properties of these boron nitride structures, the SIESTA software code was used, which is based on the time-dependent perturbation theory. By running the program and producing an EPSIMG file in its output, it has been determined that the information related to the imaginary part of the dielectric function which yield to absorption process, can be found. By using imaginary component of electrical permeability, and Kramers-Kronig equations, the real component of electrical permeability can be found [7-12]. Therefore, reflection coefficient, absorption coefficient, and refractive index can be determined with considering the real and imaginary parts of dielectric function.

There is a polarized incident light in the direction of the z axis (perpendicular to the plane of the structure) for all present structures and the energy range was also chosen from 0-10 eV for studying the optical properties, as discussed in details in the next sections.

3. Results and discussion

3.1. Structural Properties

Fig. 1 shows BN- monolayer structure after relaxation. As shown in Fig. 1(a), the unit cell of this structure is specified, so that the unit cell of this structure consists of two atoms (one boron atom and one nitrogen atom). The h-BN monolayer structure can be seen like a planar and perfectly flat structure, in where, the bending value of zero is calculated. The bond length for B-N and bond angles of B-N-B and N-B-N are 1.45 Å, and 120°, respectively. To ignore the interaction between adjacent layers, we put an empty layer of 10 Å in the z-axis direction. By these points, the total energy of the relaxed structure of -386.68 eV was obtained. By repeating the unit cell in the direction of the x and y axes, the structure of boron nitride monolayer is formed, and its relaxed structure is shown in Fig.1 (see Fig. 1(a) from the top view and 1(b) from the side view, respectively).

The structure of boron nitride bilayer after relaxation is shown in Figure 2. As shown in Figure 2(a), the unit cell of this structure consists of four atoms (two boron atoms and two nitrogen atoms). By repeating the unit cell in the direction of the x and y axes, the structure of boron nitride bilayer is formed, and its relaxed structure is shown in Figures 2 (a) and (b) from the top and the side view, respectively. It is clear from relaxed structure of h-BN, that it is a planar and perfectly flat structure.

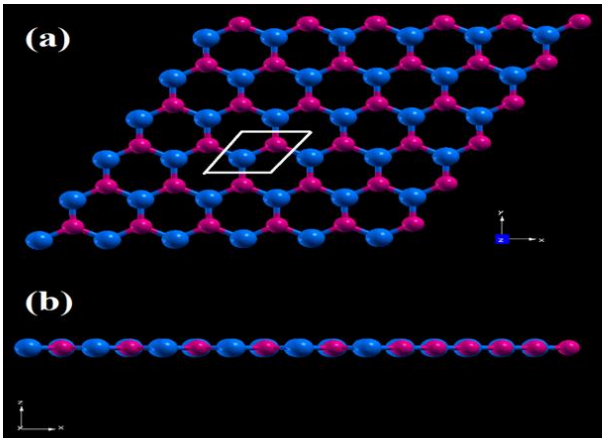

Fig. 1. Structure of boron nitride monolayer after relaxation from a) top view and b) side view.

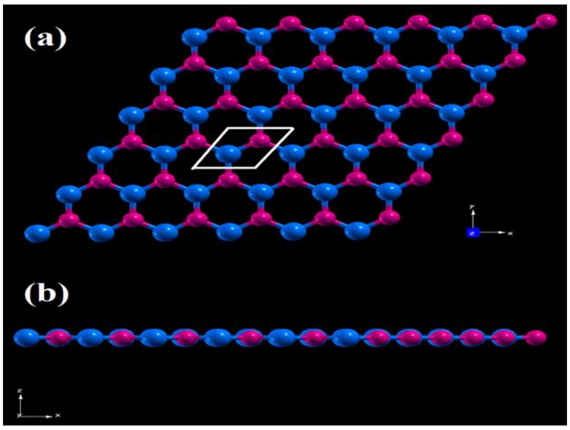

Fig.2. Bilayer structure of boron nitride after relaxation from a) top view and b) side view.

The bending value for BN monolayer is zero. The distance between the layers of 3 Å was chosen. The bond length for B-N and bond angles of B-N-B and N-B-N are 1.45 Å, and 120°, respectively. These values are exactly equal to the values obtained for the monolayer. The total energy of the relaxed structure is found -771 eV, which is more negative than the total energy obtained for the monolayer structure. This finding indicates that the bilayer structure is more stable than the monolayer structure.

The same procedure is done for bulk structure of h-BN after relaxation (See Fig. 3). As reported in Ref. [14], the bulk structure of BN is more stable than that for AB state. This is why we chose AB arrangement of atoms in the unit cell as AB. In this arrangement, as shown in Fig. 3(a), four atoms are located in the unit cell, with 3 Å interlayer. The bond length between N-C is 1.45 Å, which is in agreement with the reports of other researchers [15]. The degree of bending of the layers is zero, and the boron nitride planes in the bulk state are perfectly flat, just like the monolayer and bilayer structures. The bond angles of B-N-B and N-B-N is 120°. These values are exactly equal to the values obtained for the mono- and bi-layer. The total energy of the relaxed structure after relaxation is 773.51 eV, which is much larger than the total energy of the structure in the monolayer and bilayer states. As expected from bulk structure, this point shows that the bulk structure is more stable than the mono- and bi- layer structure, as found with other researchers [16-19].

3.2. Electronic Properties

Fig. 4 through Fig. 9, reveals the mono-, bi- layer, and bulk electronic band structures, and total density of states for these structures in the high symmetry directions in 1BZ (the first Brillouin zone). With using the results of SIESTA calculations, and plotting the results by *Qtiplot* software, and considering Fermi energy (E_F) =0 eV, all three boron nitride structures show semiconducting behavior. The band gap values of the monolayer, bilayer, and bulk are 4.55 eV, 4.50 eV, and 4.40 eV, respectively. Mono-, and bi-layer have direct band transition, meaning no effect of phonon. The transitions occur at K point for these structures, as found in Refs. [20,21], whilst indirect transition, which should phonon taken into account for the bulk structure of BN, happens in the K-M path. The results of band structure and total density of states are in agreement with each other. In the research published by Wickramaratne *et al.* in 2018 [22], it has also been observed that the boron nitride monolayer has the highest value of band gap and its band gap is direct and located at the K point. As the number of layers increases, the energy of the band gap decreases, the larger value of band gap energy can be due to the use of the GW approximation. As reported in [22-24], the GGA approximation calculations normally give us lower value of the band gap energy compared to experimental results. The results obtained in the present work, compared to the results obtained in Refs. [12-18], show that the present finding is also semiconducting and with a better and more accurate bandgap. In the cited works, their results indicate that the band gap values of all sheeted forms of h-BN are about 4.96 eV, whilst here it is in the range of 4.40-4.55 eV. Band gap energy of the present work is a function of the layer and bulk structure, it is reported in [12] that band gap energy depends, for instance, on x- (parallel) and or z- (perpendicular) direction with a gap of about 2.92 eV and 6.73 eV, respectively. Their findings demonstrated a semiconductor characteristics, too.

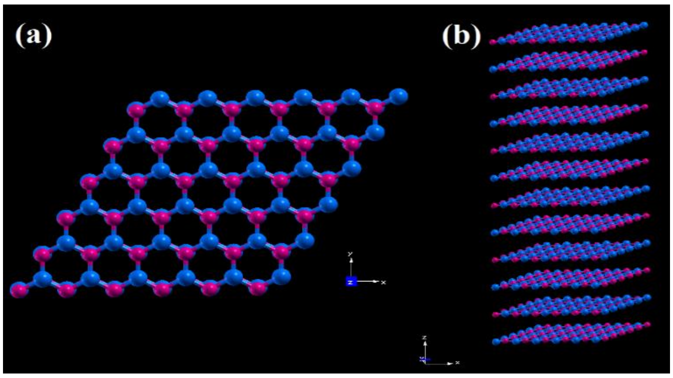

Fig.3. Bulk structure of boron nitride after relaxation from a) top view and b) side view

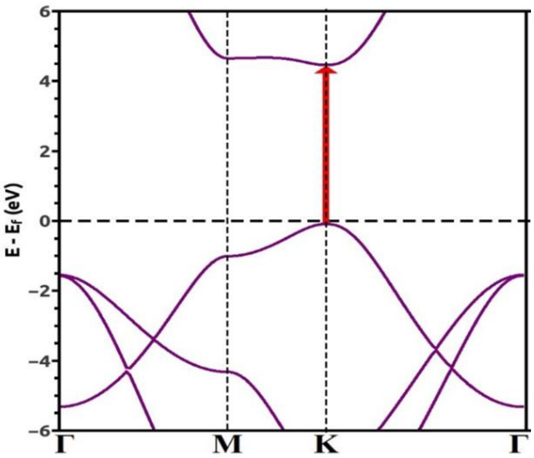

Fig.4. Band structure of boron nitride monolayer.

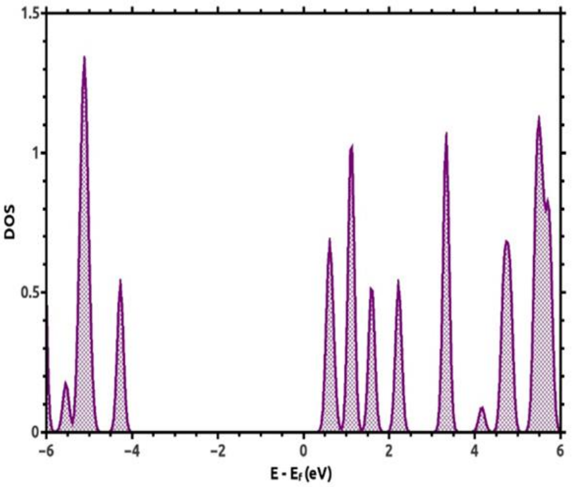

Fig.5. Total density of states of boron nitride monolayer.

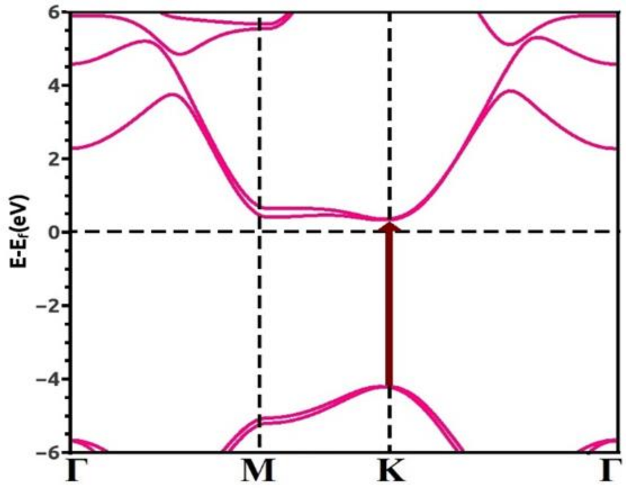

Fig.6. Band structure of boron nitride bilayer.

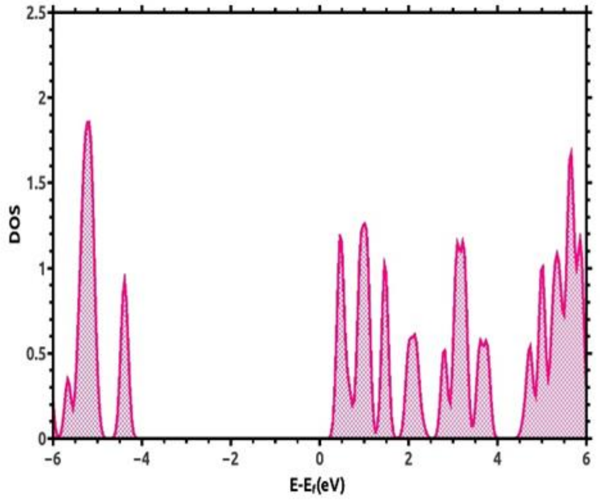

Fig.7. Total density of states of boron nitride bilayer.

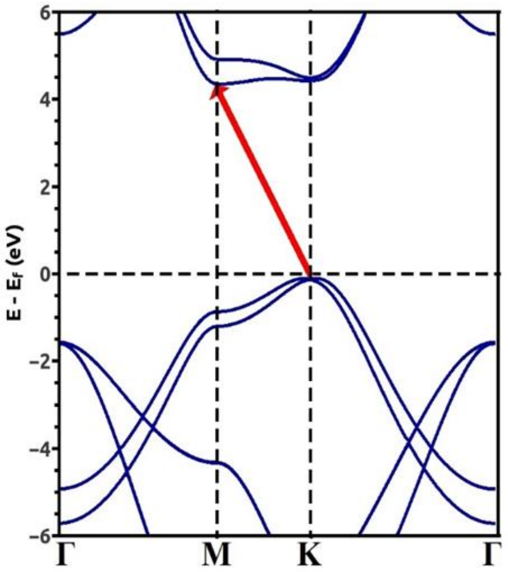

Fig.8. Band structure of bulk boron nitride.

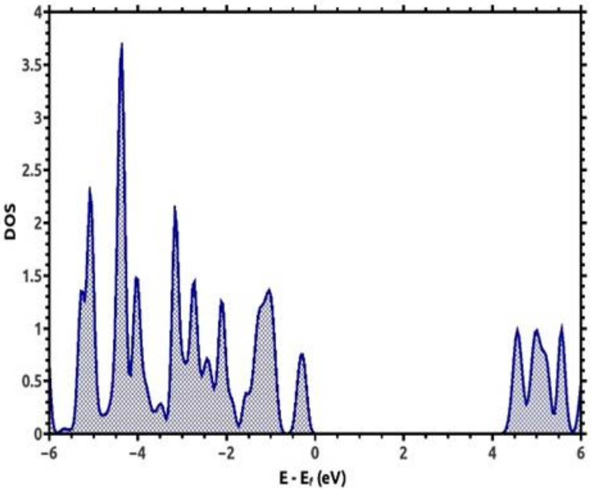

Fig.9. Total density of states of bulk boron nitride.

3.3. Optical Properties

As stated before, both imaginary (Fig. 10) and real components (Fig. 11) of dielectric function are of importance, in that imaginary component of dielectric function gives some information about absorption. Left-hand material has also negative value of permeability coefficient [24]. The incoming photon energy on three structures of BN with polarized in the direction of the z axis exhibit that the imaginary and real components of the dielectric function represent the amount of loss and scattering processes, respectively. On the other hand, the imaginary component of the dielectric function describes the inter-band transfer of excited electrons at band gap, whilst the main peak in the real part of the dielectric function is related to the first optical absorption between the conduction and valence bands. There is no significant different behavior of the dielectric function for monolayer and bilayer structures. Negative value of real component of dielectric function is shown in Fig. 11, meaning a left-hand structure could be formed and/or the excited field is in the opposite direction of the external field.

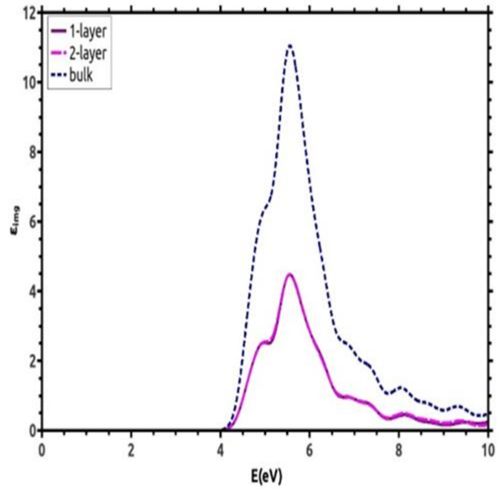

Fig.10. Imaginary part of the dielectric function of bulk, monolayer, and bilayer structures of boron nitride.

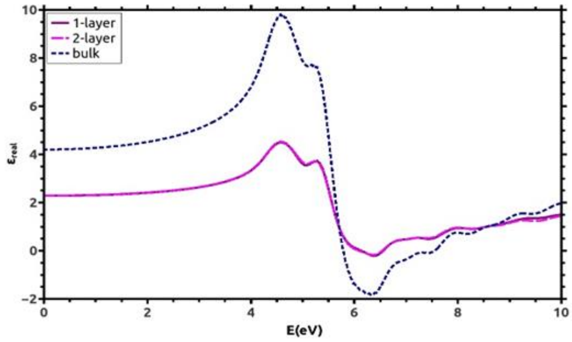

Fig. 11. Real part of the dielectric function of bulk monolayer and bilayer structures of boron nitride

There is a relation between dielectric, permittivity functions, and absorption and reflection coefficients. Figures 12 and 13, represent the above mentioned parameters for bulk, monolayer, and bilayer structures of BN. In this regard, some allowed transitions may happen between valance band (with E_V energy) and conduction band (with E_C energy) through absorption of incoming photon energy (if equal and/or higher than E_C-E_V energy). The transition threshold energy of all three bulk, monolayer, and bilayer structures of boron nitride is more than band gap energy of 4 eV, meaning that electrons can be excited by receiving a minimum energy greater than the band gap energy and experience an optical transition. In all three structures, no absorption is observed in the visible region, and the first absorption peak for all three structures is observed at an energy of about 6 eV. The absorption spectrum of monolayer and bilayer structures coincides with each other, but it is more intense in the bulk state. These results are consistent with the reports of Abedi Ravan *et al.,* [25]. They reported that the first absorption peak for mono layer of BN is located at the energy of 5.85 eV, without any dominated peak of absorption in the visible region. By studying the reflection diagram, it can be seen that, in general, the magnitude of reflection of all investigated structures at different energies is very small. The first reflection peak for all three structures is also seen at an energy of about 6 eV. If the energy of incoming photon energy on the sample structure be higher than the band gap energy, the electrons can be excited and experienced an inter band transition [23].

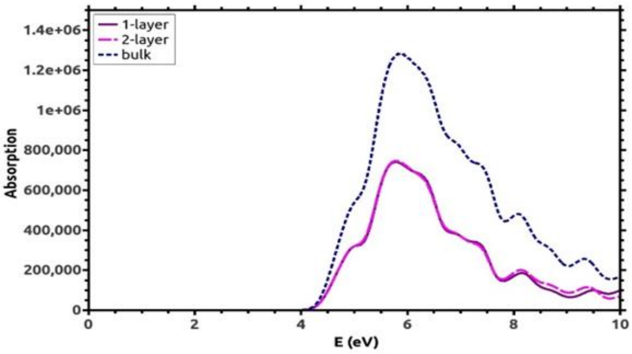

Fig. 12. Absorption spectrum of bulk, monolayer, and bilayer structures of boron nitride.

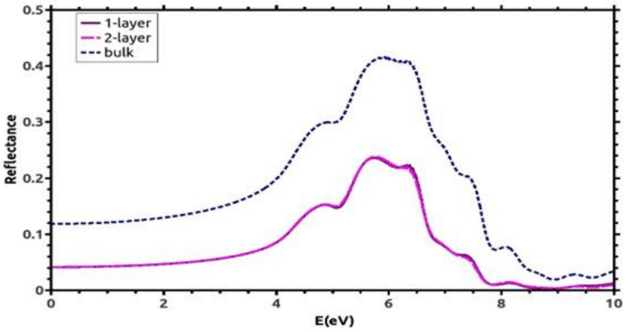

Fig. 13. Reflection spectrum of bulk, monolayer, and bilayer structures of boron nitride.

As shown in Fig. 14 (compared to Fig. 10), the optical transition of three BN structures (bulk, monolayer, and monolayer structures of boron nitride), the peaks in imaginary part of dielectric function indicate that the maximum optical transitions are seen for electrons at the energies where most absorptions occur. The refractive index (see the presented data in Table 1) for bulk – BN is much higher than that for mono- bi- layer of BN (the refractive index of mono layer and bilayer is the same, equal to 1.51). There is a little bit difference between the present data (n=1.51) and reported value in Ref. [25], where n was 1.2. The difference is because the research by Abedi Ravan *et al.* was done using the Quantum Espresso software, which uses plane waves as the basis set, while in the present research the quasi-potential approximation is used for the basis set in the SIESTA [25].

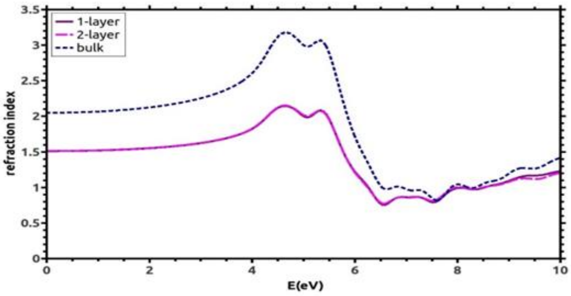

Fig. 15 Real part of the refractive index of bulk, monolayer, and bilayer structures of boron nitride.

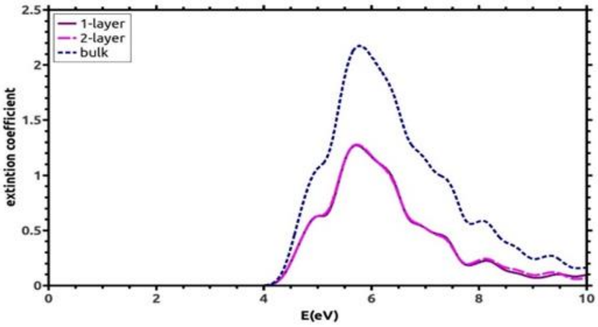

Fig. 16. Imaginary part of the refractive index of bulk, monolayer, and bilayer structures of boron nitride.

Table 1. Refractive refractive index of bulk, monolayer, and bilayer structures of boron nitride

Structure	Static refractive index
Monolayer	1.51
Bilayer	1.51
Bulk	2.05

4. Conclusion

In the present work, the optical, nano-structural, and electronic properties of monolayer, bilayer, and bulk structures of boron nitride have been studied with using the SIESTA computational code in the framework of the density functional theory and using the generalized gradient approximation (GGA-PBE). The obtained results show that BN has a planar and flat structure in all three states of monolayer, bilayer, and bulk, and the bending of the structure is also zero. The bond length and bond angles are almost the same in all three cases. There is a band gap energy about 4.55 eV, 4.50 eV, and 4.40 eV, for mono- bi-layer and bulk of BN, respectively, and thus they show semiconducting behaviors.

The obtained results also indicate that as the number of layers increases, the band gap energy reduces due to the quantum confinement effect. Comparison of the total energy of the relaxed structures shows that the total energy in the bulk state is more negative than that in the monolayer and bilayer states, which indicates the greater stability of the bulk structure compared to the monolayer and bilayer. Some parameters such as; dielectric function, absorption coefficient, reflection coefficient, and refractive index of these three structures are also studied. The results show higher refractive index of bulk than that of mono- and bi- layer structures. The main peak in the real part of the dielectric function is related to the first optical absorption between the valence and conduction bands, which is observed at an energy of about 6 eV. These semiconductor samples can be used as an element of the future of electronic and optoelectronic devices due to their suitable dielectric behavior, which for example needed in the complementary metal insulator semiconductor transistors.

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