Study the Electronic Properties of Boron Nitride Diamondiod Nanostructure using Ab-initio DFT

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Study the Electronic Properties of Boron Nitride Diamondiod Nanostructure using Ab-initio DFT

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Abstract. The first principle of density functional theory using PBE/6-31(d) base sets and the generalized gradient approximation (GGA) has been used to investigated the electronic properties of III-V BN. This included the energy gap, density of state, density of bond length and density of dihedral angle. The energy gap of quantum confinement depended on the size effect and the shape effect. B-N bond lengths of diamondoids were found around the bulk experimental value at 1.56 Å. Tetrahedral angles centred around the ideal bulk zinc-blende value at 109.47 degrees, while dihedral angles were distributed around the ideal bulk zinc-blende values at ±60 and ±180 degrees. All results were compared to experimental bulk values and illustrated that diamondoids were representative of bulk structure.

1. Introduction

Diamondoids are a type of molecule and nanocrystal, which are fractions of nano synthesizing procedures of diamond and zinc-blende materials. However, these molecules must be separated from other types of molecules, which is the case for carbon diamondoids separated from petroleum [1]. Because of the unique physical properties of boron compounds, such as low density, extremely high thermal conductivity, wide band-gap and a large resistivity, there has been much research interest over the past few years [2]. An modulation estimation of different properties from the molecular to the nano and bulk-scales is required in order to understand how to apply these materials to nanotechnology. The new collection of molecules will increase the number of atoms of varying sizes, referred to as diamondoids [3]. Researchers consider III-V semiconductors to be the most interesting type of material, due to unique characteristics and behavior [4]. For these reasons scientists have studied the materials using both first principle calculations for accuracy and density functional theory (DFT) for successfully handling many properties, especially within an electronic structure [5].

2. Theory

Boron nitride (BN) nanocrystal structures were built starting with the smallest BN molecules and diamondoids, including linear molecules (BNH₆), BN-cyclohexane (B₃N₃H₁₂), BN-diamantane (B₇N₇H₂₀), BN-tetramantane (B₁₁N₁₁H₂₈), BN-hexamantane (B₁₃N₁₃H₃₀) and BN-octamantane (B₂₀N₂₀H₄₂). The number of cages in the diamondoids was clear from the designation of the latter four. To complete the energy range and vibrational spectra, the first two molecules (which are not diamondoids) were added [6]. Figure. 1. shows the molecules and the diamondoid structures. Density functional theory was used, due to its successful handling of many properties, especially with an electronic structure. However, the Kohn-sham DFT was an insufficient method, because of its deficiencies concerning the gap issue and the long-range interaction approximations [7].
3. Results and Discussion

Figure 2. shows the energy gap, HOMO and LUMO levels as a function of the number of B and N atoms. The energy gap decreased from 6.07 eV to 4.08 eV as the size of BN diamondoids increased. This decrease correlated to vicissitudes by means of the non-spherical shape of the diamondoids. This also applied for HOMO and LUMO levels that encountered the same vicissitudes. HOMO and LUMO levels are approximations to ionization energy and electron affinity, respectively. The results are in agreement with other literature [8, 9].

Figure 3. shows the distribution of bond lengths in BN-diamantane and BN-octamantane. The main reasons for the nonequivalent bond lengths were the distance of the atoms from the surface and bonding with either one or two H atoms. The dashed line indicates the experimental value of the BN bulk bond length at 1.56 Å. The smallest bond length was the N-H bond with a sharp peak at 1.01 Å. This value is in agreement with the literature on this bond. The sharpness of this bond peak was due to the localized nature of the bond, since it was between two high electron affinity elements; i.e. N and H. The second bond peak was between B and H. Unlike the N and H bonds, this bond was between a metal and a nonmetal, which resulted in a relatively delocalized bond with several peaks. The value of this bond was subtended from the values in the literature [10]. The last peak at 1.56 - 1.65 Å was for the B–N bonds in BN-diamantane and BN-octamantane. These B-N bonds were between the previous two bonds when considering the degree of delocalization, since N was higher affinity than H.

Figure 4. illustrates a comparison between the density of tetrahedral angles in BN-diamantane and BN-octamantane. In bulk, far from the surface, all tetrahedral angles should have a value 109.47°. From Figure 4.a and b, the highest peak of BN-diamantane was at 110°, while that of BN-octamantane was at 109.4°. Tetrahedral angles of octamantane were much nearer to the ideal value 109.47° [11] than in diamantane. This was due to the effect of surface reconstruction on all atoms in BN-diamantane (all the atoms were bonded to the surface hydrogen atoms), and it had the same effect on some of the atoms in BN-octamantane.

Similarly, all dihedral angles should have one of the following values in the bulk zinc-blende structure: -180°, -60°, 60° and 180° [12]. While this might be true for the angles -180° and 180° in BN-octamantane in Figure 5.b, it was not true for the angles -60° and 60°. For BN-diamantane in Figure 5.a, the situation improved for the angles near -60° and 60°, moving closer to ideal values.

“The difference between the energy gap of the smallest diamondoids” was considered in the present work; i.e. BN-diamantane and BN-octamantane diamondoid nanocrystal in Figure 6. Energy levels were nearly discrete in BN-diamantane. As the number of energy levels increased, the discrete behavior in BN-diamantane turned into a nearly continuous band in BN-octamantane. The energy gap reduced from 5.18 eV in BN-diamantane to 4.08 eV in BN-octamantane.

4. Conclusions

BN diamondoids are molecular/nano-particles with small surface effects that have an electronic structure as near as possible to those of the bulk zinc-blende. The results showed that diamondoids had small surface relaxation effects from bond lengths, tetrahedral angles and dihedral angles. The energy gap and bond lengths were very close to those of the bulk counterparts. B-N bond lengths were affected by surface reconstruction. The shortest B-N bond was between the atoms that were not connected to surface hydrogen atoms. Tetrahedral and dihedral angles moved toward the ideal zinc-blende values as the size of the diamondoids increased. The energy gap decreased as the size of the BN diamondoid nanostructure increased.
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Figure 1. “Geometrically optimized (a) linear molecules(BNH$_6$) (b) BN-cyclohexane(B$_3$N$_3$H$_{12}$) (c) BN-Diamantane(B$_7$N$_7$H$_{20}$), (d) BN- Tetramantane(B$_{11}$N$_{11}$H$_{28}$)(e) BN- Hexamantane(B$_{13}$N$_{13}$H$_{30}$) (f) BN-Octamantan(B$_{20}$N$_{20}$H$_{42}$)"
Figure 2. “Energy gap, HOMO and LUMO levels as a function of total number of B and N atoms for BN molecules and diamondoids nanostructure.”

Figure 3. “Distribution of bond lengths in (a) BN-diamantane and (b) BN-octamantane. The dashed line represents the experimental value of the BN bulk bond length.”
Figure 4. “(a) Density of tetrahedral angles in BN-diamantane and (b) Density of tetrahedral angles in BN-octamantane. Dashed line represents ideal value of zinc-blende structure at 109.47° [11].”

Figure 5. “(a) Density of dihedral angles in BN-diamantane and (b) Density of dihedral angles in BN-octamantane. Dashed lines show ideal value of this angle in bulk in zinc-blende crystals i.e. (60° or 180°) [12].”
Figure 6. “(a) Density of states of BN-diamantane and (b) density of states of BN-octamantane.”