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Designing Two-Dimensional Dodecagonal Boron Nitride†

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Two-dimensional dodecagonal boron nitride is designed via first principles calculations. Calculations unveil that the proposed two-dimensional dodecagonal boron nitride is energetically stable and less dense than what is observed with hexagonal and octagonal configurations of two-dimensional boron nitride. Furthermore, it is found that modifying the atomic configuration of two-dimensional boron nitride can tune the band structure. In particular, a direct bandgap of 5.2 eV is observed for two-dimensional dodecagonal boron nitride while a direct bandgap of 5.79 eV and an indirect bandgap of 5.20 eV are observed for the hexagonal and octagonal configurations,respectively. Thus, tailoring atomic configurations demonstrates the possibility to tune the electric band structures of two-dimensional materials.

The development of two-dimensional materials has offered an alternative way of designing functional materials[1–6]. Two-dimensional materials consist of a single layer of atoms where their high surface-to-volume ratio results in unique physical and chemical properties that differ from the bulk states of the atoms[7]. In particular, the properties of two-dimensional materials are strongly coupled with their structures and the presence of defects[8,9]. One can therefore consider the properties of two-dimensional materials to be tunable by tailoring the structures and defects of the two-dimensional material.

Here, an allotrope of two-dimensional boron nitride is explored in terms of first principles calculations. Two-dimensional boron nitride has a large bandgap, making it an electrical insulator[10–12]. More importantly, two-dimensional boron nitride is reported to form various structures such as hexagonal, pentagonal, and octagonal configurations where the electronic and optical properties are different per configuration[13,14]. Given these examples, an allotrope with a more complex configuration- two-dimensional dodecagonal boron nitride- is investigated in order to understand the changes in electrical properties.

Grid based projector augmented wave (GPAW) method within the first principles calculations is implemented to design two-dimensional dodecagonal boron nitride[15]. Exchange correlation of Perdew–Burke–Ernzerhof (PBE) and GLLB-sc is used for structural relaxation and band structure, respectively[16,17]. Grid spacing is set to 0.18 Å. 8x8x1 special k points of the Brillouin zone sampling as well as spin polarization calculations are used[18]. 6 Å of vacuum is applied for the Z direction. Bader charge analysis is implemented to calculate the charge transfer between N and B atoms[19].

Vienna ab initio simulation package (VASP)[20] with the projector-augmented wave potential method is used to check the dynamical stability of the structure. The exchange-correlation interaction is treated by using PBE form[16]. The cutoff energy for the plane-wave-basis set is set of 450 eV. The vacuum spacing is kept of 24 Å between the image surfaces. The conjugate gradient method is used to obtain equilibrium lattice parameters and the Hellmann-Feynman forces on each atom are allowed less than 10^{-7} eV/A. The energy convergence parameter to break the self-consistent loop is set to 10^{-8} eV. To obtain phonon band structure and related thermodynamic properties, PHONOPY[21] is combined with VASP for calculating phonon dispersion. Ab initio molecular dynamics (AIMD) simulation within Nose-Hoover thermostat is performed in order to see the thermal stability[22].

The binding energy (E_b) per atom is calculated as Equation 1:

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$$E_b = (E_{2D-BN}) - m\frac{E[BulkB]}{36} - n\frac{E[Ngas]}{2} \quad (1)$$

where m and n are the number of B and N atoms in two-dimensional boron nitride, and E_b is then divided by the total number of atoms. Note that negative energy indicates an exothermic reaction.

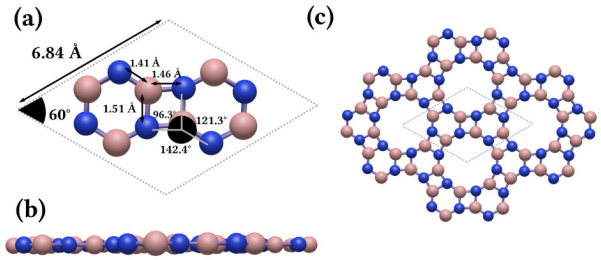

Fig. 1 The structure of 2 dimensional dodecagonal boron nitride (a)top view, (b) side view, (c) repeated case. Color code: Blue;N, Pink;N.

Two-dimensional hexagonal, octagonal, and dodecagonal boron nitride are explored via first principle calculations. Structural and electronic properties of two-dimensional hexagonal, octagonal, and dodecagonal boron nitride are collected in Table 1 while the atomic model of two-dimensional dodecagonal boron nitride is shown in Figure 1. Note that details pertaining to structural information and Bader charge analysis are collected in Supporting Information. Bond distance in two-dimensional hexagonal and octagonal boron nitride is calculated to be 1.45Å and 1.48Å(1.41Å), respectively, and are found to have good agreement with previously reported bond distances[14]. Here, two-dimensional dodecagonal boron nitride is designed by modifying two-dimensional hexagonal boron nitride as shown in Figure 1. In particular, the dodecagonal configuration is designed by placing six hexagonal configurations and six square configurations as shown in Figure 1 (c). Although binding energy of the dodecagonal configuration is 0.42 eV and 0.09 eV higher than the hexagonal and octagonal configuration, respectively, the dodecagonal configuration is an energetically stable structure. Lattice constant is calculated to be 6.84Å while having a rhombus configuration with angles of 60° and 120° where bond lengths are calculated to be 1.41Å, 1.46Å, and 1.51Å as shown in Figure 1 (a). Bader charge analysis shows that B atoms are negatively charged by 2.32 electrons while N atoms are positively charged by 2.32 electrons. It is interesting that the dodecagonal case is less dense than the hexagonal and octagonal cases as the number of atoms per unit is calculated to be 0.26 atoms/Å^2 for the dodecagonal case while the number of atoms per unit for the hexagonal and octagonal cases are calculated to be 0.32atoms/Å^2 and 0.33atoms/Å^2, respectively.

The electronic structures of two-dimensional hexagonal, octagonal, and dodecagonal boron nitride are then investigated. Two-dimensional hexagonal boron nitride is calculated to have a large bandgap of 5.79eV, showing good agreement with a previously-reported experimental measured bandgap of 5.9eV[23].

Table 1 Structural and electronic properties of two-dimensional hexagonal, octagonal, and dodecagonal boron nitride. D_{bond}: Bond distance, E_{bind}:Binding energy (eV/atoms), V_B: Average charge transfer from B (electrons), V_N: Average charge transfer from N (electrons), E_{KS}:Kohn-Sham band gap (eV), E_{KS+DXC}:Fundamental band gap of GLLB-sc (eV) where DXC is derivative discontinuity, N_{atoms}:Number of atoms per unit area (atoms/Å^2).

	Hexagon	Octagon	Dodecagon
D_{bond}	1.45	1.41, 1.48	1.41,1.46,1.51
E_{bind}	-1.27	-0.94	-0.85
V_B	2.28	2.33	2.32
V_N	-2.28	-2.33	-2.32
E_{KS}	5.79	5.20	5.20
E_{KS+DXC}	7.88	7.20	7.19
N_{atoms}	0.32	0.33	0.26

Note that the Kohn-Sham band gap without derivative discontinuity presents bandgaps similar to experimental bandgaps. Thus, two-dimensional hexagonal boron nitride can be concluded to act as an electrical insulator. On the other hand, the octagonal configuration results in a bandgap of 5.20 eV as shown in Table 1, thereby demonstrating that the bandgap can be narrowed by modifying the configuration of two-dimensional boron nitride. In the case of the dodecagonal configuration, it is interesting to see that that bandgap is calculated to be 5.20eV, which is same bandgap reported for the octagonal configuration. Hence, two-dimensional dodecagonal boron nitride also behaves as an electric insulator.

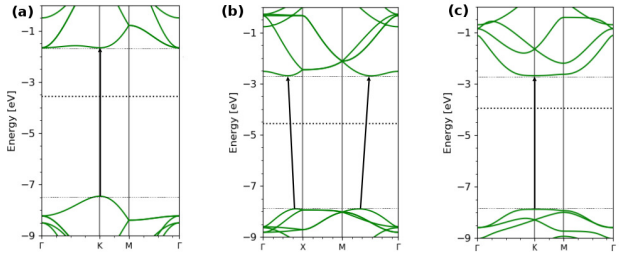

Fig. 2 The band structure of two-dimensional (a) hexagonal, (b) octagonal, and (c) dodecagonal boron nitride.

Further detailed analysis of the band structures are investigated. Band structures of two-dimensional hexagonal, octagonal, and dodecagonal boron nitride are shown in Figure 2. Note that projected density of states and total density of states for two-dimensional hexagonal, octagonal, and dodecagonal boron nitride are also shown in supporting information. One can see that band structures are varied depending on the configuration of two-dimensional boron nitride. Figure 2 demonstrates that hexagonal and dodecagonal configurations have direct band gaps while the octagonal configuration has an indirect bandgap.

Phonon dispersion of 2 dimensional dodecagonal boton nitride is calculated using phonopy and VASP. (3x3x1) supercell of the structure with 5x5x1 special k-point mesh are used/. Figure 3 (a) illustrates the calculated phonon band structure and corresponding atom projected vibrational density of states of the dodecagonal boron nitride structure. As can be seen, there are thirty

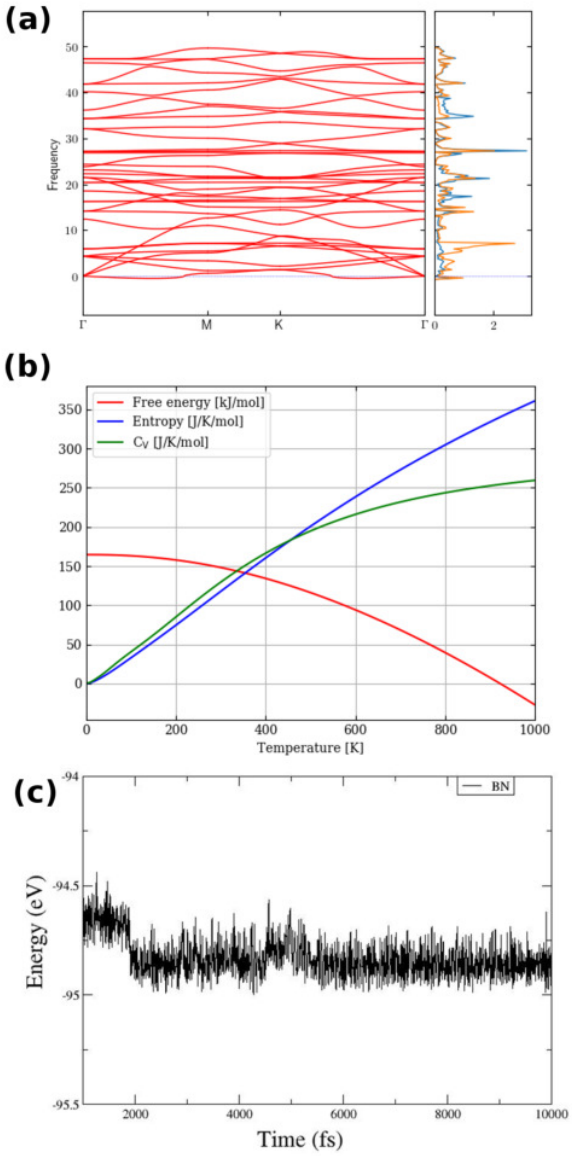

Fig. 3 (a):Phonon dispersion, (b)Changes of thermodynamic variables against to the increased temperature, and (c)ab initio molecular dynamics of time vs energy at 300K, in 2 dimensional dodecagonal boron nitride.

six separated phonon branches in the phonon band structure and three of them are acoustical and thirty three of the remaining are optical branches. The highest transverse optical mode is located around 50 THz which shows the robust of the material.There is a small imaginary frequency for out of plane acoustical mode (ZA) between Γ to M and K to Γ high symmetry points. This suggests that two-dimensional dodecagonal BN may be dynamically unstable. Given that two-dimensional dodecagonal BN is a meta-stable form compared to hexagonal BN, which acts as the ground state structure, it is possible for two-dimensional dodecagonal BN to exist at defect sites of two-dimensional hezagonal BN based on its dynamic instability.

As can be seen at the bottom panel of Figure 3 (b), the thermodynamic variables such as free energy, entropy and heat capacity change dramatically below 400 K. Free energy of 2 dimensional dodecagonal boton nitride is almost fixed between 0-200K and it decreases with increasin temperature and goes to negative values after of 900K. As expected, the entropy of 2 dimensional dodecagonal boton nitride increases with temperature. Volumetric specific heat C_v is also calculated. It is seen that when T<400 K, the heat capacity depends on temperature and according to the third law of thermodynamics, C_v also goes to zero while the temperature goes to zero and at high temperatures, C_v tends to the DulongâĂŞPetit limit. Futhermore, ab initio molecular dynamics (AIMD) is also performed to evaluate the thermal stability. Figure 3 (c) shows that energy fluctuations at 300k are minimum after 10s, suggesting that 2 dimensional dodecagonal boron nitride is potentially thermally stable. Thus, these results suggest that two-dimensional dodecagonal BN is a thermally stable material with potential dynamical instability.

In summary, two-dimensional hexagonal, octagonal, and dodecagonal boron nitride are investigated using first principle calculations. In particular, two-dimensional dodecagonal boron nitride is designed and proposed by placing six hexagonal configurations and six square configurations. The dodecagonal structure is energetically stable where it is less dense than ones observed for the hexagonal and octagonal configurations. Electronic structure analysis indicates that two-dimensional dodecagonal boron nitride has a direct bandgap of 5.20eV, and hence acts as an electric insulator. More importantly, investigations demonstrate that modifying the configuration of two-dimensional boron nitride not only allows one to tune bandgap but also affects whether materials behave as the direct or indirect bandgap of the two-dimensional material. Therefore, this work provides insight towards how the atomic configuration of two-dimensional materials may play a key role when tailoring the physical and chemical properties of a two-dimensional material.

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