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Prediction of a new graphenelike Si₂BN solid

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While the possibility to create a single-atom-thick two-dimensional layer from any material remains, only a few such structures have been obtained other than graphene and a monolayer of boron nitride. Here, based upon *ab initio* theoretical simulations, we propose a new stable graphenelike single-atomic-layer Si₂BN structure that has all of its atoms with sp^2 bonding with no out-of-plane buckling. The structure is found to be metallic with a finite density of states at the Fermi level. This structure can be rolled into nanotubes in a manner similar to graphene. Combining first- and second-row elements in the Periodic Table to form a one-atom-thick material that is also flat opens up the possibility for studying new physics beyond graphene. The presence of Si will make the surface more reactive and therefore a promising candidate for hydrogen storage.

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Because of the surge of interest in two-dimensional (2D) materials, fueled by the discovery of graphene [1], the possibility of growing novel single-layer forms of stable sp^2 -bonded phases of materials other than carbon has attracted much scientific interest. The unique qualities of 2D materials, such as their reduced dimensionality and symmetry, lead to the appearance of phenomena that are very different from those of their bulk material counterparts. Two-dimensional materials offer opportunities for new fundamental studies to address single-layer scale differences in interfacial electron-electron and electron-phonon couplings; excitonic and other quasi-particle properties; the effects of defects and the substrate; the influence of doping, strain effects, and electric fields; mechanical properties; quantum size effects; and edge effects in transport [2,3].

A graphenelike structure can also be formed by combining boron and nitrogen, which, like carbon, belong to the first row of the Periodic Table. The resulting sp^2 -bonded single-layer hexagonal boron nitride (BN) structure is a wide-band-gap semiconductor with a gap of 5.8 eV [4]. Furthermore, stoichiometric combinations of C, B, and N have also been used to propose hybrids of graphene and BN [5]. The restrictive nature of the optimization performed for these structures, however, does not allow one to affirm their stability with any certainty. More recently, a silicon analog to graphene called silicene has been the subject of investigations [6]. Similarly, a germanium monolayer has also been synthesized [7]. However, these layers were found to be organized into a puckered hexagonal lattice configuration rather than a flat monolayer [8]. Very recently, stripping 2D layers of phosphorene from black phosphorus has been reported [9].

In this work we propose a new class of hexagonal graphenelike lattice with an sp^2 -bonding configuration consisting of Si, B, and N. The structure consists of Si-Si-B-N arranged in a single layer in which each Si atom has a Si, B, and N nearest neighbor, while each B (N) has two Si atoms and one N (B) atom as nearest neighbors (Fig. 1). This arrangement clearly avoids the formation of energetically unfavorable B-B and N-N bonds while optimizing the number of Si-Si and B-N bonds, with the latter being the strongest ones. The unit cell (inset to Fig. 1) contains eight atoms and the structure has inversion symmetry.

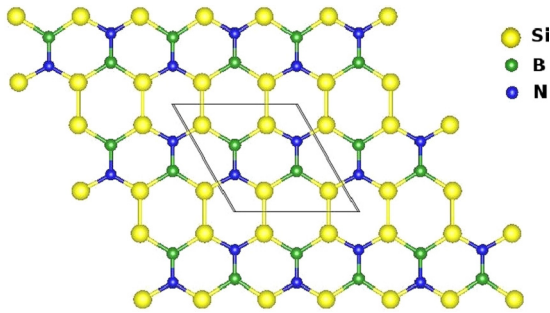
In our *ab initio* density functional theory (DFT) simulations we use the Heyd-Scuseria-Ernzerhof (HSE) [10] hybrid exchange-correlation functional, which features exact exchange. The HSE exchange-correlation functional uses an error function screened Coulomb potential to calculate the exchange portion of the energy in order to improve computational efficiency, especially for metallic systems. All our *ab initio* calculations were performed using the Vienna *Ab Initio* Simulation Package (VASP) electronic structure computer code [11]. A plane-wave cutoff energy of 500 eV was used. A $5 \times 5 \times 1$ Monkhorst-Pack [12] k -point mesh was used and all structures were relaxed without imposing any symmetry constraints. The electronic iterations convergence criterion used was 10^{-6} eV. The optimization of atomic positions (including full cell optimization) was allowed to proceed until the force on each atom was less than 5 meV/Å. As a test of the present method we have optimized a monolayer of pristine hexagonal BN. A B-N bond length of 1.44 Å was obtained, in very good agreement with the experimental value of 1.45 Å [13].

The fully optimized structure is shown in Fig. 1. The differences in the Si-Si, Si-B, Si-N, and B-N bond lengths result in a considerable amount of structural stress and the lack of in-plane isotropy under 120° rotations found in graphene and BN.

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FIG. 1. The HSE optimized Si_2BN structure.

In Table I we list the formation energy of the Si_2BN structure and compare it with those for graphene, BN, and silicene using the HSE functional. These energies were obtained for the eight-atom unit cells in each case. As can be seen in the table, the formation energy of Si_2BN lies in between the other three experimentally produced structures.

We further investigate the stability of the Si_2BN structure by calculating the phonon frequencies and verifying that they are real. The presence of imaginary frequencies is an indication of structural instability. The phonon band-structure calculations were performed using the HSE functional. The calculated phonon spectrum and total phonon density of states (DOS) [14] are shown in Fig. 2. Conventionally, any imaginary frequency of the unstable phonon mode is shown as a negative frequency. As shown in the figure, there are no negative frequencies, thus confirming the stability of this structure. The phonon spectra were also calculated using a different *ab initio* method [the generalized gradient approximation (GGA) of the DFT (DFT/GGA) and the Perdew-Burke-Ernzerhof exchange-correlation functional [15] as implemented in the VASP code] and also showed no negative frequencies, thus providing a further confirmation of its stability.

The stability of the structure was further tested using *ab initio* molecular dynamics simulations at high temperatures using the DFT/GGA theory making use of the N - P - T ensembles of the VASP code. The simulations were run at 1000 K for 12 ps and no breaking of the bonds was seen, indicating a high degree of stability.

We have also investigated two other possible planar structures that can be created with Si, B, and N while avoiding the formation of energetically unfavorable B-B and N-N bonds. These are shown in Fig. 3. In the structure of Fig. 3(a) a zigzag chain of Si atoms is connected to zigzag chains of BN on both sides. In the structure of Fig. 3(b), however,

TABLE I. Formation energies (at 0 K) using the HSE functional for the four 2D structures, each consisting of eight-atom cells. The formation energy for Si_2BN (at 0 K) is calculated using the formula $\Delta E = E(\text{Si}_2\text{BN}) - 2E(\text{Si}) - E(\text{B}) - E(\text{N})$.

Structure	Energy (eV)
graphene	-84.95
BN	-81.70
silicene	-38.20
Si_2BN	-50.38

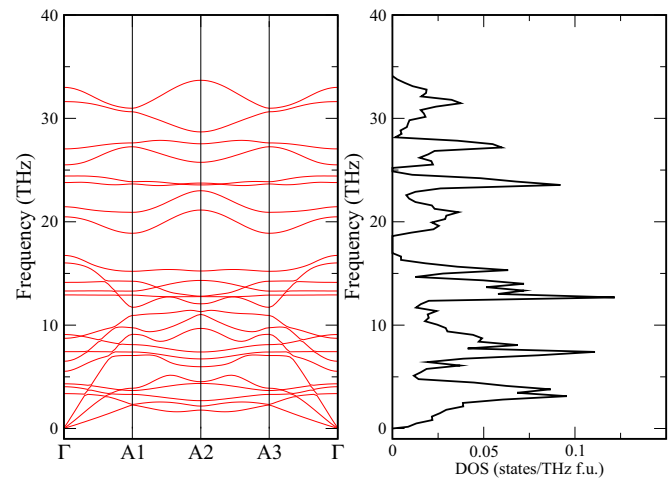


FIG. 2. Phonon dispersion relation (left) and total phonon density of states (right) for the Si_2BN structure obtained using the HSE hybrid functional. The symmetry points Γ , A1, A2, and A3 (rectangular Brillouin zone) are $(0,0,0)$, $(2\pi/a,0,0)$, $(2\pi/a,2\pi/b,0)$, and $(0,2\pi/b,0)$, respectively. The absence of any negative frequencies indicates structural stability.

each Si atom has one Si atom and two B or two N atoms as nearest neighbors. Our DFT simulations resulted in a severe out-of-plane buckling and instability (bond breaking) for both structures. The instability of the structure of Fig. 3(a) is understandable given the fact that the Si-Si (2.13 Å) bond length is significantly larger than the B-N bond length (1.47 Å) and so a zigzag Si-Si chain cannot be matched to a zigzag B-N chain due to the large differences in the bond lengths. The instability of Fig. 3(b) is caused by the unfavorable electronic arrangement resulting from each Si atom having either two B or two N neighbors.

In Fig. 4 we show the DFT results for the band structure and DOS as obtained with the HSE hybrid potential for the Si_2BN unit cell in Fig. 1. As can be seen in the figure, the structure is metallic.

The Brillouin zone of the single-layer Si_2BN differs from that of graphene and BN due to the absence of a hexagonal symmetry. This lifts the degeneracies of the π bands at the symmetry points Γ , A1, and A3 (Fig. 4). Furthermore, the lack of a twofold rotation axis in the plane (C_{2v} symmetry) also eliminates any band crossings at other symmetry points between Γ , A1, and A3. All these result in the separation of bands seen in the band structure. It should be noted, however,

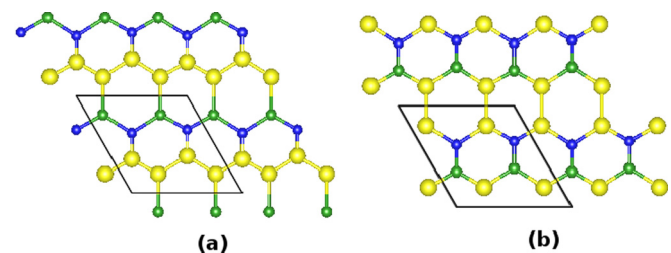


FIG. 3. Two additional structural models considered for the Si_2BN layer. The DFT simulations for these resulted in out-of-plane buckling and distortions.

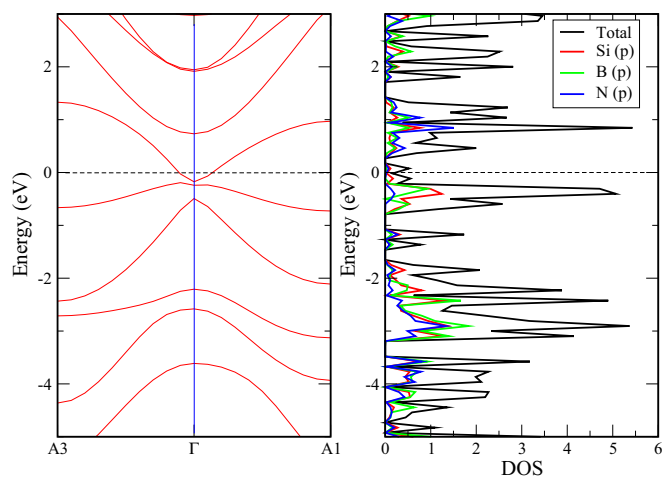


FIG. 4. Calculated band structure (left) and DOS (right) obtained with the HSE hybrid functional for the Si_2BN monolayer eight-atom unit cell in Fig. 1. The Fermi energy is indicated by the dashed lines.

that despite the drastic reduction in symmetry, the Si_2BN monolayer still retains the inversion symmetry, which causes it to be metallic [5]. From the DOS plot we find that the contribution to the states at E_F comes from the p states of Si and N.

Next we propose that the Si_2BN sheet can be rolled up to form nanotube structures as done with graphene and BN. The presence of three chemical species combined with the large covalent radius differences offers intriguing possibilities

for nanotube formation that are distinct from carbon and BN nanotubes. For example, each of the zigzag and armchair nanotubes could be formed with two different arrangements of the constituent elements. Furthermore, the anisotropic geometry of the hexagonal Si_2BN sheet offers a variety of ways of rolling the sheet into chiral nanotubes with a wide range of structural, electronic, and chemical properties. For example, since the bond angles deviate from the ideal 120° on the nanotube wall, this could result in an increase of the $\pi^*-\sigma^*$ orbital hybridization and alter the reactivity of the nanotube walls with bonding strengths varying with the bonding sites. Based on the charge distribution analysis, the Si sites are expected to be more “sticky” (reactive) compared to other sites. This would indicate a chemistry distinct from those of C and BN based nanotubes. The electronic structure analysis using DFT reveals both zigzag and armchair nanotubes to be metallic, suggesting them to be one-dimensional metals.

In conclusion, we have presented a study of a new class of single-atom-thick graphenelike material formed from Si_2BN with unusual characteristics using *ab initio* simulations. Considering the fact that Si (a second-row element from the Periodic Table) does not tend to form a stable flat 2D structure, it is quite surprising that Si_2BN can exist as a stable single-layer structure that is also flat. Due to the 2D nature, the Si_2BN sheet can be flexible and strong and could exhibit other properties common to 2D materials such as high electron mobilities, tunable band structures, and high thermal conductivities. The inherent metallicity with a sufficient DOS at E_F allows for a substantial increase in conductivity by doping or by structural rearrangement (for example, induced by pressure).

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