Nanopores in Bernal-Stacked Hexagonal Boron Nitride

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When single-layer \textit{h}-BN is subjected to a high-energy electron beam, triangular pores with nitrogen edges are formed. Because of the broken \textit{sp}\textsuperscript{2} bonds, these pores are known to possess magnetic states. We report on the magnetism and electronic structure of triangular pores as a function of their size. Moreover, in the Bernal-stacked \textit{h}-BN (AB-\textit{h}-BN), multilayer pores with parallel edges can be created, which is not possible in the commonly fabricated multilayer AA'-\textit{h}-BN. Given that these pores can be manufactured in a well-controlled fashion using an electron beam, it is important to understand the interactions of pores in neighboring layers. We find that in certain configurations, the edges of the neighboring pores remain open and retain their magnetism, and in others, they form interlayer bonds. We present a comprehensive report on these configurations for small nanopores. We find that at low temperatures, these pores have near degenerate magnetic configurations, and may be utilized in magnetoresistance and spintronics applications. In the process of forming larger multilayer nanopores, interlayer bonds can form, reducing the magnetization. Yet, unbonded parallel multilayer edges remain available at all sizes. Understanding these pores is also helpful in a multitude of applications such as DNA sequencing and quantum emission.

I. INTRODUCTION

Low dimensional materials allow for a plethora of applications that are not available for bulk (three-dimensional) materials. In particular, creating holes in two-dimensional (2D) materials enable applications such as molecular sieving, metamaterials and quantum emission [1–5]. By controlling the size, shape and/or distribution of holes in a 2D material, researchers can tailor the system for a desired application. An example of such an application is DNA sequencing through nanopores (holes that are up to several nm in size), which would enable fast and precise sequencing of single unbroken DNA chains [6–10]. Nanopores also spontaneously form in 2D materials, so, understanding their properties is important in itself. In this study, we investigate the properties of triangular pores in single-layer hexagonal boron nitride (\textit{h}-BN) and their interactions with pores in neighboring layers, which is largely determined by the stacking sequence and pore alignment. We focus primarily on Bernal-stacked \textit{h}-BN which can house parallel-edged triangular pores in neighboring layers because of the lack of rotation between the layers [11].

Layers of \textit{h}-BN can be stacked in different ways, resulting in different material properties [12–15]. The trivial stacking sequence [Figure 1(a)], named the AA stacking, includes no in-plane shift or rotation between consecutive layers. When this stacking is repeated to form bulk \textit{h}-BN, columns of B atoms and columns of N atoms in the out-of-plane direction are created. We include this unobserved high-energy stacking sequence in our study as a reference. It has an interlayer distance of 3.64 Å. Common synthesis methods yield a bilayer stacking sequence [Figure 1(b)], named the AA’ stacking, in which each layer is a 60° rotated copy of the preceding layer, resulting in columns of alternating B and N atoms in the bulk [16]. An alternative stacking sequence, in which there is no rotation between consecutive layers [Figure 1(c,d)], named the AB stacking (a.k.a. Bernal stacking), was recently reported in large quantities [15]. Until a robust and reproducible method for growing AB-\textit{h}-BN was discovered, it was only observed in rare cases [17–19]. In AB-\textit{h}-BN, three types of columns repeat to form the bulk material: (1) alternating B and N atoms; (2) alternating B atoms and hollow sites; (3) alternating N atoms and hollow sites [Figure 1(c,d)]. Many computed properties of AB-\textit{h}-BN are close to those of AA’-\textit{h}-BN, such as interlayer distance (AB: 3.09 Å vs. AA’: 3.11 Å), indirect band gap (AB: 4.43 eV vs. AA’: 4.41 eV) and dielectric tensor [15].

An infinite sheet of single-layer \textit{h}-BN is a wide-gap insulator, yet, computational studies have shown that its edges and pores exhibit a rich collection of electronic and magnetic properties [11, 20–25]. The unpaired electrons that occupy dangling \textit{sp}\textsuperscript{2} hybrid orbitals at edges and pores result in magnetism which is absent in the pristine sheet. The most commonly observed vacancies in \textit{h}-BN are boron monovacancies, formed when a single boron atom is removed from the sheet [Figure 2]. These vacancies can be created by a high-energy electron beam in a transmission electron microscopy (TEM) chamber. As the beam is applied for longer periods of time, the vacancies grow into larger pores in predictable ways [15, 25–28]. The pores have three nitrogen-terminated zigzag edges that form an equilateral triangle. In the large pore limit, these edges approximate the edges of an infinite sheet (N-edge), which is the most common edge type in \textit{h}-BN [16, 29–35], and has magnetic properties that we elucidated in a previous computational study [11]. In the current study, we first investigate the spin configurations of nanopores in single-layer \textit{h}-BN. We then discuss what happens to the pores in multilayer \textit{h}-BN. In the common
recently utilized to generate ferroelectricity bilayer property of AB-

versa. Hence, the distinction between these two types becomes equivalent to the bottom layer in AB2, and vice versa. Therefore the B (N) atom of the top layer is aligned with the B atom in the bottom layer, whereas the B atom in the top layer is aligned with the hollow site of the bottom layer. Therefore the B (N) atom of the top layer is not in the same physical environment as the B (N) atom of the bottom layer. Given a starting bottom layer, the top layer may be formed in two distinct ways, shown in Figure 1(c,d), which we name AB1 and AB2, respectively. The top layer in AB1 then becomes equivalent to the bottom layer in AB2, and vice versa. Hence, the distinction between these two types within the AB stacking is meaningful when we are considering a well-defined bottom layer and a well-defined top layer, as we will in the discussion below. This property of AB-h-BN separates it from AA′-h-BN and was recently utilized to generate ferroelectricity bilayer h-BN.

II. METHODS

We conduct density functional theory (DFT) calculations within the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE GGA) [39], using the QUANTUM ESPRESSO software package with norm-conserving pseudopotentials [40, 41]. The plane-wave energy cutoff for the pseudo Kohn-Sham wavefunctions used is 80 Ry. For a 1 × 1 unit cell of h-BN, we use a 12 × 12 × 1 Monkhorst–Pack k-point mesh to sample the Brillouin zone [42], and choose k-point meshes accordingly for larger unit cells. A ∼14 Å of vacuum is placed between the copies of the 2D system along the out-of-plane direction to isolate the sheets. In order to include the interlayer van der Waals interactions, we include a Grimme-type dispersion correction [43]. All atomic coordinates are relaxed until the forces on all the atoms are less than 10−3 Ry/a0 in all three Cartesian directions, where a0 is the Bohr radius.

III. RESULTS

A. Nanopores in monolayer h-BN

We start with a survey of the possible spin configurations in the boron monovacancy in the single layer h-BN. Throughout this article, we label pores as “NTn”, where “NT” stands for “nitrogen-terminated”, and n is the number of nitrogen atoms on each edge of the triangle. Thus, a boron monovacancy is denoted as NT1. In Figure 2(a-d), we present the atomic structure of NT1 in its various magnetic configurations. Figure 2(a) is obtained by running a collinear calculation, resulting in a structure with 3-fold symmetry. The structures in Figure 2(b-d) are obtained by relaxing the atoms further with noncollinear spin channels and different starting configurations. All three of these configurations have lower energies compared to the collinear structure, as listed in Table I, and are local minima in the configuration space. We find that the 3-fold symmetric NC(30,150,270) structure has the lowest energy, but only by ∼ 2 meV, compared to NC(90,90,270). Interestingly, the latter configuration is a triplet of atomic structures, where there are two shorter N–N distances (2.70 Å) and a longer N–N distance (2.78 Å). At regular temperatures (20 K < T < 500 K), we expect both the NC(30,150,270) and NC(90,90,270) pores to be present in single layer h-BN with pores with only trace amounts of NC(90,90,90). To the best of our knowledge, previous studies have only identified NC(90,90,90) [25, 44–46]. Although no probing of the local magnetism of edges or pores in h-BN has been reported, ferromagnetism has been shown to occur in h-BN at room temperature [47], which can be attributed to the existence of edges and pores in regular h-BN samples.

The next smallest triangular pore is NT2, which is obtained by removing three borons and one nitrogen from the system (Figure 2(e)). In this pore, the corner nitrogens approach each other and form dimers, resulting in a collinear electronic structure (|nt↑ − nt↓| = 0 everywhere), as reported previously [25, 45].
Figure 2. Atomic structures of the collinear (a) and noncollinear (b-d) spin configurations in the nitrogen-terminated pore with 1 nitrogen per edge (NT1); atomic structure of the nitrogen-terminated pore with 2 nitrogens per edge (NT2); spin-resolved projected densities-of-states (PDOS) plots for the noncollinear NT1 pores (f-h); PDOS plot for the NT2 pore (i). The isosurface plots for absolute magnetization with the isovalue $|n_\uparrow - n_\downarrow| = 0.02 |e|/a_0^3$ are included in the atomic structure pictures. The direction of magnetization on each magnetized atom is denoted by a red arrow, and the structures are labeled by these directions at the bottom right corner of panels (b-d). The atoms on whose orbitals the densities-of-states are projected are labeled in (a). The Fermi energy is set to the mid-gap in cases where there is a band gap.

|                  | NT1 (3)               | NT2 (0)               |
|------------------|-----------------------|-----------------------|
|                  | Collinear NC(90, 90, 90) | Collinear NC(90, 90, 270) | Collinear NC(30, 150, 270) |
| $\Delta E$ (eV) | $\equiv 0$             | $-0.138$              | $-0.185$              | $-0.187$              | $\equiv 0$              |
| ES type          | metal                 | half-metal            | magnetic SC           | nonmagnetic SC        | nonmagnetic SC          |
| $E_{gap\uparrow}$ (eV) | 0                     | 4.64                  | 0.67                  | 0.68                  | 1.94                    |
| $E_{gap\downarrow}$ (eV) | 0                     | 0                     | 0.55                  | 0.68                  | 1.94                    |

Table I. Total energies, electronic state types and band gaps of the NT1 and NT2 nanopores. Refer to the text for the explanation of the labels in the second row. The total energies are with reference to the collinear configuration and presented per edge N atom, for instance, $\Delta E$ of and NT1 configuration is computed by subtracting the energy of the collinear configuration from it and dividing by 3 (the number of edge N atoms).

Looking at the electronic structures of the NT1 pores (Figure 2(f-h)), we observe that the NC(90,90,90) pore is a half-metal, i.e. the majority spin channel is insulating and the minority spin channel is a metal, the NC(90,90,270) pore is a magnetic semiconductor and the NC(30,150,270) pore is a nonmagnetic semiconductor, although the electronic structures of the latter two configurations are very similar. The antiferromagnetic state is a semiconductor with a gap of 0.51 eV. Because the spin configuration and the electronic structure are closely linked, these pores may be useful in various spintronics applications [48–54]. As seen in Figure 2(i), the electronic structure of the NT2 pore is a nonmagnetic semiconductor with a larger gap (Table I). We present the atomic and electronic structures of larger pores in single layer h-BN (NT3–NT8) in Figures S1–S6. The key information for these larger pores is summarized in Table II. In each case, we fully relax the pore in a collinear calculation, and then run a self-consistent field calculation with two initial spin configurations: where all the edge spins are set as parallel (P), and where consecutive edge spins are set as antiparallel (AP). We note that we have confirmed in a few test cases that in these larger pores, further relaxations with noncollinearity cause negligible changes in atomic positions. In Figures S1–S6, the magnetization in the real space is only plotted for the P configurations (the AP configurations have equivalent plots with alternating sign). In Table II, we also include the case of the N-edge.
taken from Ref. [11], which may be interpreted as the limiting case NT∞.

From the results in Figures S1–S6 and Table II, we make a few observations: (i) The corner N atoms remain dimerized in these larger pores and thus have no magnetic moment. This causes the sequence of the absolute value of the magnetic moments to be approximately 3μB, 0, 3μB, 6μB,... for the NT1, NT2, NT3, NT4,... pores. (ii) For the NTn pores with n ≥ 2, the energy differences between P and AP spin configurations is smaller compared to NT1 and the N-edge. The comparison with NT1 can be explained by the isolation provided by the dimerized corner N atoms. The comparison with the N-edge may be due to the fact that these pores are still small, and many of the edge N atoms lack nearest and next-nearest neighbors to interact with, as opposed to the infinite edges (we know that both nearest and next-nearest neighbor interactions are important for the spin dynamics in this system, cf. [11]). This near degeneracy of different spin configurations would be advantageous in applications that rely on magnetic switching. (iii) The P configurations are consistently half-metals, and the AP configurations are either magnetic semiconductors (MSC) or nonmagnetic semiconductors (NMSC), depending on the number of available magnetic sites (written in parentheses in the first row of Table I and the first column of Table II). The band gap of the NMSC configurations gradually increases with the pore size, approaching the value of the N-edge (0.51 eV). (iv) The positions of the in-gap states for the AP configurations depend on the pore size. Because the pore size can be controlled by the duration of the applied electron beam [27, 28], it should be possible to engineer the desired in-gap states at a desired location on the h-BN layer.

### B. Nanopores in bilayer h-BN

When nanopores are created on multilayer h-BN, they tend to begin on the top layer and then propagate into the layers underneath [25, 28]. As a first step in understanding nanopores in multilayer systems, we present results on nanopores on the top layer of bilayer h-BN, where the bottom layer remains as a full sheet. In Figures S7–S22, we present the atomic and electronic structures of pores NT1–NT4 in a single sheet stacked on a full sheet using AA, AA′, AB1 and AB2 stacking sequences. For NT1, NT3 and NT4 pores, parallel (P) and antiparallel (AP) spin configurations are run without further relaxation of the atomic positions (NT2 remains fully spin-unpolarized), and the magnetization in the real space is only plotted for the P configurations (the AP configurations have equivalent plots with alternating sign). Our findings are also summarized in III. In general, the behavior of the pores in the bilayer remains very similar to their behavior in single h-BN sheets, although the small shifts in the energy levels. However, the magnetized regions around the edge N atoms do not lie entirely parallel to the sheet for the larger pores (NT3 and up), instead, these spin-polarized dangling orbitals point away from the bottom sheet by an angle θ, which is listed for each case in the table.

Once a nanopore begins to form in the top layer of multilayer h-BN, the second layer becomes exposed the electron beam, giving rise to progressively larger and deeper (in terms of the number of layers) pores [25, 28]. In the next part of our work, we investigate the coexistence of small pores in both layers of bilayer h-BN in order to elucidate the early stages of this process. In Figures S23–S24, we present the NT1 pores on both layers of bilayer h-BN (in this case, AB2 stacking is identical to AB1 so it is not presented separately). The NT1 & NT1 configurations are uncoupled in the sense that the pores in the neighboring layers do not interact beyond the already present van der Waals forces. We note here that for the

|      | ΔE (eV) | ES type | E_{gap} (eV) |
|------|---------|---------|--------------|
| NT3 (3) | P | -0.230 | half-metal | 0.41, 0 |
|        | AP | -0.229 | MSC | 0.15, 0.09 |
| NT4 (6) | P | -0.235 | half-metal | 0.46, 0 |
|        | AP | -0.242 | NMSC | 0.31, 0.31 |
| NT5 (9) | P | -0.220 | half-metal | 0.58, 0 |
|        | AP | -0.225 | MSC | 0.18, 0.29 |
| NT6 (12) | P | -0.225 | half-metal | 0.70, 0 |
|        | AP | -0.236 | NMSC | 0.33, 0.33 |
| NT7 (15) | P | -0.226 | half-metal | 0.72, 0 |
|        | AP | -0.227 | MSC | 0.25, 0.41 |
| NT8 (18) | P | -0.226 | half-metal | 0.95, 0 |
|        | AP | -0.229 | NMSC | 0.36, 0.36 |
| N-edge [11] | P | -0.218 | half-metal | 4.56, 0 |
|        | AP | -0.184 | NMSC | 0.51, 0.51 |

Table II. Total energies, electronic state types and band gaps of the NT3–NT8 nanopores. Refer to the text for the explanation of P and AP labels. The total energies are with reference to the collinear configuration and presented per edge N atom, for instance, ΔE of an NT3 configuration is computed by subtracting the energy of the collinear configuration from it and dividing by 9 (the number of edge N atoms). The numbers in parentheses in the first column denote the number of magnetic N atoms for each pore.
NT1 & NT1 configurations, we have checked for potential interlayer coupling of spins by running a comprehensive collection of spin polarization combinations. We have not found a noteworthy difference in energies beyond a simple summation of the energies of spin configurations in each layer.

As the next step in the process for the AB stacking, we remove the 3 N atoms of the bottom layer that are exposed in addition to the 1N atom on the top layer. This results in the configuration in Figure S25, which is an unusual defect structure where three B atoms in the bottom layer move inward within the plane and form a trimer. This magnetic semiconductor has the band gaps (0.59, 0.43) eV in the two spin channels. We note that this structure is not an artifact of symmetry and seems to be robust with respect to atomic position perturbations.

For larger pores in bilayer h-BN, we focus on the AB stacking. As discussed above, due to the relative 60° rotation between consecutive layers in the AA’ stacking, multilayer pores become irregularly shaped, whereas the AB stacking allows for nested and aligned pores [25]. As the next step in AB1-h-BN, we assume that the NT2 pore has formed in the top layer, and then we remove the boron in the center of the exposed area in the bottom layer (cf. Figure S13). This results in the NT2 & NT1 structure presented in Figure S26, which is also an uncoupled structure (half-metal, \( E_{\text{gap}} = 1.95 \) eV). Removing the 6 exposed nitrogens from this configuration results in our first coupled structure, presented in Figure 3(a). This 3-fold symmetric structure is a magnetic semiconductor with 6 interlayer B–N bonds. Forming the NT2 & NT1 structure in AB2-h-BN is possible in two different ways by removing a boron from either the center or the corner of the exposed area in the bottom layer (cf. Figure S14).

In both cases, we get uncoupled structures that are presented in Figures S27–S28 (both magnetic semiconductors with the band gaps (0.46, 0.44) eV and (0.49, 0.26) eV, respectively). Finally, we present the NT2 & NT2 structures in the AA and AB1 stacking sequences in Figures S29–S30, both of which are uncoupled and nonmagnetic semiconductors with the band gaps 1.53 eV and 1.74 eV, respectively (AB2 is equivalent to AB1).

We then move to the NT3 pore in the top layer of AB1-h-BN. Removing one of the three exposed borons in the bottom layer (cf. Figure S17) results in the NT3 & NT1 uncoupled structure (Figure S31), which is a half-metal with \( E_{\text{gap}} = 0.64 \) eV. Similarly, the NT3 & NT2 structure in AB1-h-BN is also uncoupled (Figure S32) but metallic. Next, we remove the remaining exposed nitrogens so that all the atoms in the bottom layer that are exposed when the top layer has an NT3 pore are removed. This results in the structure in Figure 3(b) which has reflection symmetry and 9 interlayer B–N bonds, and is a magnetic semiconductor. An interesting effect occurs when the NT3 & NT3 structure in AB1-h-BN is set up and relaxed, in which two edge nitrogens in the bottom layer detach from their neighbors and form an \( \text{N}_2 \) molecule. When the molecule is taken out of the system, the resulting coupled structure, which is metallic, is presented in Figure 3(c). Because the bottom layer has lost two nitrogens, we call this configuration NT3 & NT3*, and it has 4 interlayer B–N bonds as well as 1 interlayer N–N bond. This structure demonstrates that not all nested NT\( n_1 \) & NT\( n_2 \) pores are possible in their expected stoichiometry in bilayer and therefore multilayer AB-h-BN.
Figure 3. Atomic and electronic structures of bilayer pores in AB1-\(h\)-BN that result in coupled structures where the top layer is an NT2 or NT3 pore. (a) The NT2 & (1B6N) configuration. (b) The NT3 & (3B9N) configuration. (c) The NT3 & NT3* configuration. The isosurface plots for magnetization with the isovalue \(n_\uparrow - n_\downarrow = \pm 0.02 \frac{|e|}{a_0}\) are included in the atomic structure pictures. Top view and side view of each nanopore are stacked vertically in each panel. For the spin-resolved density of states plots in the bottom row, the Fermi energy is set to the mid-gap in cases where there is a band gap.

There are three inequivalent NT3 & NT1 structures in AB2-\(h\)-BN depending on which boron in the bottom layer is removed (cf. Figure S18). These three result in uncoupled half-metallic structures that are presented in Figures S33–S35 with \(E_{\text{gap}_1} = 0.63, 0.64, 0.66\) eV, respectively. The two inequivalent NT3 & NT2 structures in AB2-\(h\)-BN are also uncoupled and half-metallic, and presented in Figures S36–S37 (\(E_{\text{gap}_1} = 0.63, 0.61\) eV, respectively). The NT3 & NT3 structure in AB2-\(h\)-BN is equivalent to that in AB1-\(h\)-BN (Figure 3(c)). Finally, we present the NT3 & NT3 structure in the AA stacking sequence in Figure S38, which is a magnetic metal with interlayer bonding of the mid-edge nitrogens.

The largest size we have considered for bilayer \(h\)-BN in this study is the NT4 pore. We start with the NT4 & NT1 configuration in AB1-\(h\)-BN of which there are two (Figures S39–S40). Both of these are uncoupled and half-metallic with \(E_{\text{gap}_1} = 0.66, 0.69\) eV, respectively. When the bottom layer has an NT2 pore, interlayer bonds form, but not all the top edge nitrogens are bonded. This coupled configuration (NT4 & NT2) is presented in Figure S41 and is a half-metal with \(E_{\text{gap}_1} = 0.24\) eV. Enlarging the bottom layer pore one more step to set up the NT4 & NT3 structure results in the detachment of three \(N_2\) molecules and 12 interlayer B–N bonds (Figure 4(a)). By losing most of its dangling orbitals, this system, which we call NT4 & NT3*, becomes a fairly large-gap magnetic semiconductor. Next, we remove the remaining exposed nitrogens from this configuration so that all the atoms in the bottom layer that are exposed when the top layer has an NT4 pore are removed. This results in the structure in Figure 3(b) which has 12 interlayer B–N bonds and is a magnetic semiconductor. The NT4 & NT4 bilayer pore in AB1-\(h\)-BN also results in some interlayer bonding(Figure 4(c)). In this configuration, the alignment of the two edges (diagonal in Figure 4(b)) is different from the alignment of the remaining edge (horizontal in Figure 4(c)). The interlayer bonds form only at the latter
IV. CONCLUSION

We conducted a first-principles study of the nitrogen-terminated triangular nanotubes in \( h \)-BN with a special focus on Bernal-stacked \( h \)-BN (AB-\( h \)-BN). We found that the ground state of the smallest pore (B monovacancy)
is a 3-fold symmetric configuration with zero total magnetization. However, the existence of magnetic configurations that are almost degenerate with the ground state heightens the potential of magnetic switchability. For larger pores in single-layer h-BN, configurations with parallel and antiparallel neighboring magnetizations are also close in energy, indicating the likelihood of easier magnetization of these pores compared to longer edges where energy differences are larger. For bilayer configurations with pores in both layers, we find that in most cases, the layers remain uncoupled, i.e., no significant out-of-plane movement or bonding occurs. However, several structures that are expected to occur during electron irradiation do form interlayer bonds, reducing the magnetic character of the pores. We expect these types of coupled structures to occur during electron irradiation alongside the simpler decoupled structures. We also find that some nested pores are not possible in their expected stoichiometry in bilayer and therefore multilayer AB-h-BN as a result of the detachment of nitrogens by forming N₂ molecules. We hope that our results will motivate experimental studies that closely investigate the magnetic and electronic properties of these pores in h-BN, given their enormous potential in applications such as DNA sequencing.

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