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1. Introduction

Downscaling of modern integrated circuitry components to nanometric dimensions necessitates greater spatial precision in control over the electrical properties of electronic materials. This is especially true with the complexity in the structure of the device components, and with the range of device materials. In recent years, the 'wonder material' graphene has been explored intensively due to its ultrahigh room-temperature carrier mobility,^{1–4} and is touted to be the next-generation electronic material to replace silicon, since the latter is approaching its performance limits. Successful efforts have been made to induce a small bandgap of milli-eVs in the semi-metal graphene.^{5,6} On the other hand, hexagonal boron

A graphene-boron nitride lateral heterostructure – a first-principles study of its growth, electronic properties, and chemical topology[†]

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The lateral integration of graphene and hexagonal boron nitride permits the intricate design of a hybrid heterostructure in which electronic characteristics can be tuned as per the requirement of a particular application. Such laterally integrated hybrid nanostructures are investigated using density functional theory to explore their growth, electronic properties, and chemical topology. The evolution of energetics, geometry, density of states, number of charges, and electric dipole moment with carbon adatoms is delineated. In the triangular C-BN heterostructures, C atoms prefer to grow from the vertices as compared to the edges of the heterostructures due to their strong anchoring. Despite a small lattice mismatch between h-BN and graphene, the structural stability of the heterostructure depends on the number of C adatoms (i.e. stage of growth), and growth from the B-terminated BN flake appears to be preferred. The Cu substrate reduces the stability of the C-BN heterostructure. The heterostructures are metallic, suggesting that charge transfer effects from the Cu substrate play a dominant role in governing the electronic properties of the heterostructures. Electron localization and guantum theory of atoms in molecules illustrate the partial ionic-covalent character of the B-N bonds, which are less covalent than C-B/C-N bonds in the heterostructures. All in all, this study on the evolution of the characteristics of the C-BN heterostructures with growth is a vital step towards developing hybrid nanoelectronic circuitry with precisely controlled properties.

> nitride (h-BN), another two-dimensional honeycombed material, has garnered widespread interest, partially due to its graphenelike geometrical structure, with a wide bandgap of approximately 6 eV,⁷ which makes it an outstanding dielectric material. Furthermore, h-BN has superior chemical and thermal stability.⁸⁻¹¹ The distinct disparity in the electronic properties of graphene and h-BN spurred the idea of integrating them in electronic devices, in one way or another, such that the bandgap can be moderated or tuned¹²⁻¹⁴ at selective locations in the hybrid devices.

> Naturally, the next question is – how should the two materials be combined? There are numerous propositions, one of which is *via* the doping mechanism. Domains of graphene or BN can be created by doping boron and nitrogen atoms in graphene,¹⁵ or carbon atoms in h-BN,¹⁶ and hence generating a matrix of graphene and BN 'patches'. Apart from this, both materials can also be put together in its entirety of form. For example, graphene and h-BN can be grown or stacked on top of each other in various arrangements to form composite sheets (if they are of similar sizes) or vertical heterostructures^{5,17–21} (if their sizes are dissimilar), which essentially renders them as three-dimensional nanostructures. On the other hand, assimilation can also be done laterally. These in-plane heterostructures of graphene and h-BN were first synthesized by lithographical regrowth, either by regrowth of h-BN

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 $[\]dagger$ Electronic supplementary information (ESI) available: [N-terminated; (B, N) = (top, fcc)] heterostructure on a (6 × 6) Cu(111) substrate. Charge density land-scape of [B-terminated; (B, N) = (fcc, top)] heterostructure with 1C atom. Variation of formation energy, edge excess energy, and binding energy with external electric field. See DOI: 10.1039/c5tc00539f

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from the edges of patterned graphene by low-pressure chemical vapour deposition (LPCVD),²² or the converse,²³ facilitated by the highly similar lattice structure of both materials (lattice mismatch \approx 1.6%). In this paper, we refer Material A to be the material from which regrowth takes place, and the other material to be Material B. The crystalline quality of the hybrid heterostructure is contingent on that of the edges of Material A, which in turn is affected by factors characterizing the growth process, namely: (1) chamber pressure, (2) chamber temperature, and (3) feedstock gas partial pressure. In general, the quality of the nanostructure is reliant on the resolution of the lithography mask, and inconsistencies and imperfection of the technique are apt to create edge defects. In the context of lithographical regrowth, interfacial disorder between the two materials is prevalent. To circumvent this problem, the simplest and most direct way is to do without the lithography mask. Instead of LPCVD, atmospheric pressure chemical vapor deposition (APCVD) is used for the continuous growth of Material B from the edges of Material A.²⁴ To further justify the advantages of APCVD over LPCVD, irregular dendritic edges have been found in graphene by the former method,25 while the latter aids the alignment of the atoms at the edges of hexagonal graphene flakes.²⁶⁻³⁰

Interestingly, the results of growth studies show subtle disagreements over the nature of the predominant factor controlling the lattice orientation of Material B. Ref. 24 suggests that lateral templated growth can be promoted by using near-identical growth conditions for both materials. Ref. 31 presenting the heteroepitaxial growth of h-BN from fresh graphene edges by APCVD goes further to accentuate the significance of Material A (graphene), and the substrate is relatively inconsequential to the growth of Material B (h-BN).³¹ The growth of the h-BN heteroepitaxial crystal from the one-dimensional edge of the graphene seed crystal depends only on the lattice structure of graphene, and not on the underlying copper substrate. However, if the graphene seed crystal is absent, h-BN aligns itself with the copper substrate. Essentially the greater importance of the 'lateral' template (edges of Material A) in inducing lattice coherence of the two materials, with respect to the 'vertical' template (substrate), was postulated in the growth studies.

In spite of such experimental studies, there is still a substantial lack of information regarding the energetics of the in-plane graphene-BN heterostructures. Which sites do the carbon atoms prefer in the initial phase of growth, when the interface between both materials is in the process of formation? How does the lattice mismatch between the two materials, albeit how small it is, affect the structural stability of these lateral heterostructures? How does the binding energy of the heterostructures change as carbon atoms become sequentially bonded to h-BN? What effects does a substrate such as Cu have on the electronic properties of the heterostructures? These are relevant and imperative questions that have remained unanswered at this point. We embark upon addressing these questions with the help of density functional theory. Since the focus is on the heterostructures in their initial growth phase, they are hereafter more appropriately named as C-BN heterostructures. Apart from the above, energetics of the heterostructures and electronic properties such as the projected density of states (PDOS), and Bader charges are calculated. Last but not least, we analyze the electron density distribution by the electron localization function (ELF)^{32–34} and the quantum theory of atoms in molecules (QTAIM),^{35–39} and describe the character of the chemical topology in the C–BN heterostructures.

2. Computational model

A triangular BN flake (BN) deposited on a Cu(111) substrate is considered for electronic structure calculations. The (111) surface of the Cu substrate has been chosen since its lattice mismatch with BN is small at $\sim 2\%$. Note that synthesis of a triangular form of the BN flake has been reported.^{40,41} In fact, triangular flakes of other two-dimensional materials such as graphene⁴² and molybdenum disulphide $(MoS_2)^{43}$ have also been synthesized. The substrate Cu(111) is made up of three ABC-stacked layers, and arranged in the face centered cubic (FCC) structure. It is first simulated by a (4×4) supercell to investigate the initial stage of the growth process of the C-BN heterostructure. At a later stage of the growth process with full coverage of the h-BN edges with C, we consider a (6×6) supercell for final calculations. For initial calculations, the choice of a smaller (4×4) cell allows us to use our computational resources in an efficient way. Note that the flake in the (4×4) configuration is approximately 0.6 nm in length on each side of the triangle, and is comparable to that of the smallest quantum dots (\approx 0.8–1.0 nm) that have been synthesized.^{44–47} Therefore the trends and qualitative conclusions are relevant and useful to get an insight into the nucleation and structure of the material.

For the triangular BN flake/Cu(111), the initial configurations considered for calculations are (1) B-terminated; (B, N) = (top, fcc), (2) N-terminated; (B, N) = (top, fcc), (3) B-terminated; (B, N) = (fcc, top), (4) N-terminated; (B, N) = (fcc, top). 'Top' and 'fcc' are the adsorption sites of the substrate, and the B and N atoms are positioned in such a way that they are either on top of or at the fcc site of the substrate (Fig. 1). In the equilibrium configurations, B and N atoms in (2) and (3) occupy approximate commensurate positions on top of the substrate, while in (1) and (4), the atoms relax to incommensurate positions. To eliminate the effects of incommensurability, only (2) and (3) are



Fig. 1 Top view of the Cu(111) substrate, and possible adsorption sites (in purple: fcc/F; in dark blue: top/T) on the surface.

considered for further calculations. Note that our choice of configurations is guided by the fact that the growth of the C–BN heterostructure is likely to be dependent on the binding strength of C to the BN flake deposited on the Cu(111) substrate.

Calculations based on density functional theory (DFT) were performed using the VASP (Vienna Ab Initio Simulation Package) package, with the implementation of projector augmented-wave (PAW) pseudopotentials⁴⁸ (with an energy cutoff of 400 eV) and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional in the generalized gradient approximation (GGA).⁴⁹ Dispersion correction was included in the calculations by the DFT-D2 approach of Grimme.⁵⁰ The Brillouin zone was sampled with a $(9 \times 9 \times 1)$ k-point mesh using the Monkhorst-Pack scheme.⁵¹ The structures were optimized until the forces (as calculated by the Hellmann-Feynman formalism^{52,53}) were less than 10^{-5} eV Å⁻¹. In the supercell, the structure is separated from its periodic image in the direction perpendicular to the surface by a vacuum region of 12 Å. Dipole corrections were applied in the direction perpendicular to the material surface to avoid interactions between periodically repeated images.

To partition the continuous charge density among the atoms in the system, Bader's atoms in molecules theory^{35–39} is implemented, such that the atomic basin is determined at the zero flux surface around the atom. This surface is observed in the two-dimensional sense at which the charge density is at a minimum perpendicular to the system surface. Therefore the total electronic charge of each atom can be defined, and the charge among the atoms distributed.

As a prior step to depositing the flake on the substrate, the geometry of the substrate is optimized. Subsequently, the BN flake is added. In calculations of the BN flake/Cu(111) structure, the geometry of the substrate is constrained, while the BN flake is fully relaxed.

3. Initial growth pathways

The growth of the C-BN heterostructure is extrapolated such that every B or N atom at the perimeter of the BN flake is bonded with a C atom, essentially forming a complete C-BN lateral heterostructure. Fig. 2 shows the initial steps taken to simulate the growth process of the C-BN heterostructure. The relative total energies of the heterostructures with different bonding sites of C are given. For the BN flake, we define the vertices to be at the points of the triangle, while an edge is considered between two vertices. Note that [N-terminated; (B, N) = (top, fcc) and [B-terminated; (B, N) = (fcc, top)]configurations have zigzag edges that are constituted of the same type of element at the vertices and edges. Therefore the [N-terminated; (B, N) = (top, fcc)] flake is made up of 6 nitrogen atoms (3 at the vertices, and 3 at the edges), and 3 boron atoms. [B-terminated; (B, N) = (fcc, top)] flake consists of 6 boron atoms (3 at the vertices, and 3 at the edges), and 3 nitrogen atoms. The side-view of the optimized structure of the triangular BN/Cu(111) systems is presented in Fig. 3(a), (b), (e), (f) and 4(a), (b), (e), (f). The heterostructure relaxes to anchor itself



Fig. 2 Growth pathways of (a)–(d) [N-terminated; (B, N) = (top, fcc)] and (e)–(h) [B-terminated; (B, N) = (fcc, top)] lateral heterostructures. The labels and dashed lines denote the bonding sites that are considered in the study. The cross symbols mark the sites at which C cannot be bound to the heterostructure, while the labels in bold refer to the sites that are most energetically favorable. The bracketed numerals refer to the relative total energies of the C–BN heterostructures, with different bonding sites of C. Atoms in green are B, grey are N, and brown are C.

with its vertex atoms nearer the Cu substrate relative to other atoms.

Due to symmetry, some of the bonding sites of the flake are identical to those in Fig. 2, and hence are redundant in this study. For example, Site 1B is only one of the three edge sites in Fig. 2(a) and (b). The energetically most favorable sites are shown in bold in Steps 0–2, while bonds are marked with a 'cross' symbol if the C atom relaxes to occupy a position far from the initial site. The growth of C atoms from the lateral heterostructure is such that C bonding takes place at the vertices in preference over the edges. This is primarily due to the particular arrangement of the atoms in the structure. In both heterostructures, the vertex and edge atoms, which are of the same element, occupy the fcc sites above the Cu(111) substrate, whereas atoms of the other element are at the top





Fig. 3 [N-terminated; (B, N) = (top, fcc)] lateral heterostructure. (a), (e) Top-view, (b), (f) side-view, (c), (g) charge transfer plot, (inset shows a magnified view of the interface region around the C atom; the plot is calculated by subtracting the charge density distribution of the entire system by that of the substrate and the heterostructure), (d), (h) charge density landscape (top row shows the landscape with the C atom; bottom row shows the landscape without the C atom | left figures are taken through one of the central axes of the heterostructure and through the C atom; right figures are bird's eye views of the horizontal slice through the C atom). For (a)–(d), the C atom is bonded to the vertex; for (e)–(h), it is bonded to the edge. Atoms in green are B, grey are N, and brown are C. The colors dark blue, light blue, and purple are used to represent the top, middle, and bottom layers of Cu, respectively.

sites. However, a C atom bonded to the edge atom is at a top site, while it is at an hcp site if it is bonded to the vertex atom. Consequently a C atom bonded at the vertex site lies in the vicinity of three neighbouring Cu atoms and forms bonds with them. The charge transfer plot of the [N-terminated; (B, N) = (top, fcc)] (hereafter named as N-terminated) system indirectly demonstrates the formation of bonds between the C atom and the three Cu atoms (Fig. 3b, and more clearly in the inset; the plot is calculated by subtracting the charge density distribution of the entire system by that of the substrate and the heterostructure). The accumulation regions are depicted in red, while the depletion regions are in yellow. The Cu atoms that are transferring charges with the B/N atoms are numbered. For the [B-terminated; (B, N) = (fcc, top)] (hereafter named as B-terminated) system, using the same isosurface values of 0.008 e Å⁻³ (as in Fig. 3b), Fig. 4b shows a greater spatial distribution of charge transfer when the BN–C flake is bonded to the Cu substrate. When the C atom is bonded to the edge atom of the BN flake (Fig. 3e and 4e), the transfer of charges only takes place between the C atom and one Cu atom. This contributes largely to the more energetically favorable sites at 1A, 2B, and 3C shown in Fig. 2.



Fig. 4 [B-terminated; (B, N) = (fcc, top)] lateral heterostructure. (a), (e) Top-view, (b), (f) side-view, (c), (g) charge transfer plot, (inset shows a magnified view of the interface region around the C atom; the plot is calculated by subtracting the charge density distribution of the entire system by that of the substrate and the heterostructure), (d), (h) charge density landscape (top row shows the landscape with the C atom; bottom row shows the landscape without the C atom | left figures are taken through one of the central axes of the heterostructure and through the C atom; right figures are bird's eye views of the horizontal slice through the C atom). For (a)–(d), the C atom is bonded to the vertex; for (e)–(h), it is bonded to the edge. Atoms in green are B, grey are N, and brown are C. The colors dark blue, light blue, and purple are used to represent the top, middle, and bottom layers of Cu, respectively.

The charge density distribution at other regions of the heterostructure is not affected by the formation of the C–B/N bond (Fig. 3(c) and (f), 4(c) and (f)). Moreover, the three-dimensional bird's eye view shows that the charge density at the nitrogen atoms is largest, followed by that at carbon, and then at boron. Furthermore, there is no apparent difference in the charge density at a vertex N atom and one at an edge. The addition of a C atom does not significantly change the charge density in the B and N atoms. As the C–BN heterostructure is not planar, taking a horizontal slice inevitably excludes information that does not fall within that slice. In the vertical slice of the landscape, colours are assigned recursively to data points with values smaller or larger than the saturation levels defined.

However, the aforementioned provides only a visual approach. By using Bader's method to draw the atomic boundaries,^{35–39} the mean charge of the atoms in the BN/C–BN heterostructure is then more accurately probed. Contrasting the on-site charges in the heterostructure (deposited on the Cu substrate) and the triangular BN flake (without C atoms bonded to it), the change in the charges in the BN flake is then calculated, which describes the



Fig. 5 On-site charges in B and N atoms at each step of growth. (a)–(d) [N-terminated; (B, N) = (top, fcc)] lateral heterostructure; (e)–(h) [B-terminated; (B, N) = (fcc, top)] lateral heterostructure. Atoms in green are B, grey are N, and brown are C.

charge transfer effect induced by both the C atoms (if any) and the Cu substrate (Fig. 5). [Only the charges in the B and N atoms are included in this analysis to permit a direct comparison of the charges between the various structures. Note that the change in charges shown in Fig. 5(b)–(d), (f)–(h) is with respect to the BN flake (without C atoms) in vacuum.] In the N-terminated system (Fig. 5(a)), all atoms gain charges. The N atoms gain more charges than the B atoms. However in the B-terminated system (Fig. 5(e)), the N atoms lose charges, while the B atoms gain charges. Since the electronegativity of N is (3.04 on Pauling scale⁵⁴) larger than that of B (2.04), the loss of charges of N is attributed to the substrate effect.

From an inspection of the charges in the B and N atoms between growth steps, we can derive the contribution of the

charge transfer effect that originates from the bonding of C atoms to the BN flake. The change in the number of charges in the nearest neighboring atom to the C atom when the C atom is added to the flake is approximately 0.30 e for B and N atoms in the N-terminated system, whereas it is around 0.80 e in the B-terminated one. By summing up all the values in Fig. 5 in each individual step and configuration, and finding the difference between steps, we can then quantify the effective charge transfer effect induced by the bonding of C atoms: the N-terminated system gains 0.40 e in the 1st step, and 0.31, and 0.49 e in the following steps. In comparison, the B-terminated system loses 0.90 e in the 1st step, and then 0.88, and 0.87 e in the subsequent steps. Evidently, the C atoms have a larger charge transfer effect on the B-terminated system.

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4. Evolution of energetics, geometrical structure, electronic interaction, and electric dipole moment

A complete C–BN lateral heterostructure is shown in Fig. 6. The evolution of the formation energy, edge excess energy, binding energy of the heterostructure to the Cu substrate, C–N/C–B bond length, flake–substrate distance, mean charge transfer in the heterostructure (as presented in Fig. 5), and electric dipole moment with the growth of the heterostructure are tabulated in Tables 1 and 2. The formation energy is defined as the difference between the total energy of the system and the sum of the energy of its constituents,

$$E_{\rm f} = E_{\rm C-BNf/Cu} - \sum_{\alpha = {\rm Cu}, {\rm B}, {\rm N}, {\rm C}} n_{\alpha} \mu_{\alpha} \tag{1}$$

where $E_{\text{C-BNf/Cu}}$ is the total energy of the BN flake–Cu substrate system, n_{α} is the number of atoms of a particular element α , and μ_{α} is the chemical potential of that element α . The formation energy quantifies the stability of a molecule, and according to eqn (1), a more stable molecule has a more negative E_{f} . Both types of C–BN heterostructure become more stable with its growth, either in the presence of the Cu substrate (numeral without brackets) or in its absence (bracketed numerals). The substrate reduces the stability (*i.e.* smaller formation energy)



Fig. 6 Top views of the complete C–BN lateral heterostructure in the (a) [N-terminated; (B, N) = (top, fcc)], and (b) [B-terminated; (B, N) = (fcc, top)] configuration. Atoms in green are B, grey are N, and brown are C.

of the heterostructure. The binding energy of the flake is expressed as

$$\Delta E = E_{\rm BNf/Cu} - E_{\rm Cu} - E_{\rm BNf} \tag{2}$$

where $E_{BNf/Cu}$, E_{Cu} , and E_{BNf} are the total energies of the structure with the flake, without the flake, and of the flake itself. Thus, a bound flake will be associated with a negative binding energy (eqn (2)). To check whether the supercell is sufficiently large to eliminate the interaction between periodically repeated images in the x- and y-directions, we have repeated the calculation of the binding energy of the bare [N-terminated; (B, N) = (top, fcc)] heterostructure on a (6×6) Cu(111) substrate (Fig. S1, ESI[†]). The binding energy is calculated to be -1.696 eV per atom, which is less than 0.5% from that on a (4×4) Cu(111) substrate (to 3 decimal places: -1.700 eV per atom). In the initial growth phase with 1 to 3 C atoms, the binding energy of the N-terminated heterostructure decreases with an increase in the number of C atoms. This is in stark contrast to that of the B-terminated heterostructure in which the binding energy increases. However for both configurations, the binding energy in the complete C/BN form is lower than that in their initial growth phase. The formation energy and binding energy of the complete N-terminated heterostructure is lower than that of the B-terminated one. In other words, the N-terminated heterostructure is less stable, and this agrees exactly with ref. 24 which shows that there is transfer of charges from N to C, resulting in the occupation of antibonding states to form weaker interfaces.

Nevertheless, both heterostructures differ not only in the way C is bonded to the BN flake, *i.e.* C–N bonds in the N-terminated flake, and C–B in the B-terminated one, but also the sites at which the atoms are positioned on the Cu substrate. Essentially, the dissimilitude in how the characteristics of the heterostructures evolve with growth (Tables 1 and 2) reflects both the substrate effect ('vertical' template) and the edge-termination effect ('lateral' template).

We define the edge excess energy as the difference between the sum of the bond energies in the heterostructure and the

Adatoms	+0C	+1C	+2C	+3C	Complete			
Energetics								
Formation energy (eV per atom)	-3.65(-3.96)	-4.31(-5.25)	-4.85(-5.45)	-5.28(-5.67)	-5.85(-6.10)			
Edge excess energy/length (nN)	3.77	3.14	2.62	2.21	4.88			
Binding energy (eV per atom)	-1.70	-1.17	-0.69	-0.30	-0.09			
Structure								
C–N bond length (Å)	_	1.28(1.19)	1.28 (1.19)	1.27 (1.19)	1.52(1.19)			
Flake–substrate distance (Å)	1.74	1.72	1.70	1.70	1.67			
Electronic interaction								
Total charge transfer (e per atom)	0.32	0.37	0.40	0.46	0.50			
Electrostatic								
Electric dipole moment (eV $Å^{-1}$)	-0.37	-0.36	-0.30	-0.21	-0.42			

Table 1 [N-terminated; (B, N) = (top, fcc)] heterostructure deposited on a Cu(111) substrate: energetics, and structural and electronic properties. The formation energy and bond length of the heterostructure in the absence of the Cu substrate are shown in brackets

 Table 2
 [B-terminated; (B, N) = (fcc, top)] heterostructure deposited on a Cu(111) substrate: energetics, structural, and electronic properties. The formation energy and bond length of the heterostructure in the absence of the Cu substrate are shown in brackets

Adatoms	+0C	+1C	+2C	+3C	Complete
Energetics Formation energy (eV per atom) Edge excess energy/length (nN) Binding energy (eV per atom)	$egin{array}{c} -4.32 & (-4.78) \ 1.21 & -1.25 \end{array}$	-4.33 (-4.79) 0.90 -1.38	-4.36 (-4.86) 0.58 -1.42	-4.39 (-5.21) 0.27 -1.43	-6.28 (-6.49) 3.31 -0.48
Structure C–B bond length (Å) Flake–substrate distance (Å)	 1.80	1.47 (1.44) 1.75	1.45 (1.60) 1.71	1.44 (1.66) 1.68	1.56 (1.52) 1.97
Electronic interaction Total charge transfer (e per atom)	0.06	-0.04	-0.14	-0.24	-0.28
Electrostatic Electric dipole moment (eV \mathring{A}^{-1})	-0.30	-0.26	-0.20	-0.12	-0.01

sum of the bond energies in the dimer configuration,⁵⁵

$$\gamma = \frac{1}{L} \left[\sum_{\beta = B - N, C - N, C - B} n_{\beta} (E_{\beta, \text{bond}} - E_{\beta, \text{dim}}) \right]$$
(3)

where n_{β} is the number of bonds between two atoms denoted by β , $E_{\beta,bond}$ is the mean bond energy in the heterostructure, $E_{\beta,\text{dim}}$ is the bond energy in the dimer configuration, and L is the length of the edge. For the heterostructure, the mean bond energy $(E_{\beta,\text{bond}})$ is the difference in total energies of the heterostructure and its constituents divided by the number of bonds in the heterostructure. In a particular heterostructure, the same value of $E_{\beta,\text{bond}}$ is used in the derivation of the excess energy of each edge. For the dimer, the mean bond energy $(E_{\beta,\text{dim}})$ is the difference in total energies of the dimer (for example B-N or C-N) and its constituents. The bond energy of B-N, N-C, C-C, and B-C is calculated to be -4.63, -8.24, -7.11, and -4.12 eV, respectively. As there is a lattice mismatch (1.6%) between graphene and BN monolayers, albeit how small it is, the bonding of C atoms to the BN flakes will induce a non-trivial amount of in-plane strain in this nanoscale lateral heterostructure. For both configurations, the edge excess energy per unit length (hereby simplified as 'edge excess energy') is reduced with the initial growth (1 to 3 C atoms), but when the complete heterostructure is formed, there is a large significant increase in excess energy. In general, the B-terminated heterostructure has a smaller edge excess energy than the N-terminated one.

The change in average charge transfer during growth is listed in Tables 1 and 2. The gain (loss) in charges in the N-terminated (B-terminated) heterostructure increases with the bonding of C atoms to the BN flake. The net charge in the B-terminated heterostructure with 1 or 2 C atoms attached is relatively small although the binding energy is non-trivial at about -1.30 eV per atom. Likewise, although the B-terminated heterostructure has a larger charge transfer effect (Fig. 5), the change in the formation energy as it grows is generally smaller than that for its counterpart. This suggests that the charge transfer is not likely to be the dominant factor in its stability and binding strength to the substrate. However, the evolution of the electric dipole moment is reflected by the charge transfer effect; the change in electric dipole moment is greater in the B-terminated heterostructure, which is probably due to the stronger charge transfer effect induced by the C atoms as the C atoms are bonded to the BN flake.

Subsequently, the sensitivity of the energetics of the lateral heterostructures in response to an external electric field is studied (Tables S1 and S2, ESI†). The electric field is applied in the direction perpendicular to the heterostructure surface. In general, the formation energy and edge excess energy (which is calculated from the formation energy using eqn (3)) increase with the electric field strength in the positive direction. Notably, the change in the edge excess energy ranges from 5–10%. On the other hand, a direct relationship between variations in binding energy with the electric field is not observed, although the change of the binding energy with the field strength approaches 10% in a few cases.

5. Density of states

The density of states (DOS) are calculated and projected onto the atomic orbitals of boron and nitrogen in the two forms of the BN flake/C-BN heterostructure to characterize the atomic contributions to the energy bands (Fig. 7 and 8). The heterostructures at each stage of growth are metallic, suggesting the significance of charge transfer effects from the Cu(111)substrate. The x and y directions are defined within the plane of the heterostructure, while the z direction is taken to be perpendicular to the surface of the material. Only the contribution of the p_x and p_y orbitals is presented; the p_z DOS is simply the difference between the total DOS and the sum of the p_x and p_y DOS. For B, the magnitude of the in-plane p-DOS (sum of p_x and $p_{\nu})$ of B is significantly larger than that of its out-of-plane p_z -DOS at the Fermi level (Fig. 7 and 8). In comparison, for N, the magnitude of p_v -DOS is much smaller than that of p_x - and p_z -DOS. This is justified by the charge density plot at Γ and the Fermi level for the B-terminated heterostructure with 1 C atom (Fig. S2, ESI[†]). Most of the states in B and N atoms of both configurations occupy energy levels between $E_{\rm F} - 10$ eV and $E_{\rm F}$ (Fig 7 and 8). As more C atoms are bonded to the N-terminated BN flake, the B and N atoms gain more charges (Table 1), and

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Fig. 7 Atomic orbital projected density of states of [N-terminated; (B, N) = (top, fcc)] heterostructure. Zero is taken to be Fermi energy.

the DOS of both species shift to lower energies (Fig. 7). Similarly, the loss of more charges in the B-terminated BN flake with more C atoms bonded (Table 2) induces an upward shift of energies of the occupied DOS with respect to the Fermi level (Fig. 8). Strong hybridization of the occupied p_x and p_y states near the Fermi level is observed in the complete B-terminated C–BN heterostructure, but not in its N-terminated counterpart.

6. Chemical topology

The chemical bond, or more specifically, the electron density distribution between atoms can be described accurately by two tools – the first is the electron localization function (ELF),³²⁻³⁴ and the second is the Laplacian of the electron density *via* the quantum theory of atoms in molecules.³⁵⁻³⁹ The ELF is a

measure of the likelihood of finding an electron in the vicinity of a reference electron located at a particular point, with the same spin.⁵⁶ Mathematically

$$\mathrm{ELF} = \left\{ 1 + \left[\frac{C(\vec{r})}{C_{\mathrm{h}}(\rho(\vec{r}))} \right]^2 \right\}^{-1}$$
(4)

where *C* is a measure of the electron localization, \vec{r} is the radial distance from the nucleus, and ρ is the electron spin density. It ranges from 0 to 1, with it approaching 1 when *r* is within the pair region, and it is small when *r* is close to the border between two pair regions. In a homogeneous electron gas, the ELF is 0.5 at every location. The covalency of the bond is primarily delineated by the form of the charge attractors; if they are more spherically distributed around the cores of the atoms, the interaction is more ionic or highly van der Waals in nature.



Fig. 8 Atomic orbital projected density of states of [B-terminated; (B, N) = (fcc, top)] heterostructure. Zero is taken to be Fermi energy.

In a more covalent bond, the attractor is more symmetric about the cores, while still lying on the bond line connecting the cores. The number and form of the localization regions are strongly dependent on the choice of the ELF isovalue, and conventionally, an isovalue of approximately 0.80–0.85 is used for valence compounds.

In Fig. 9(a) and (b), the ELF of isovalues 0.50, 0.65, and 0.82 are plotted for the N-terminated flake/heterostructure. The ELF for the first two isovalues serves as a reference for that of isovalue 0.82. The localization region of isovalue 0.82 is slightly asymmetrical about the center point between any B–N pair (especially between the B atom and the vertex N atom in Fig. 9(a) where the region envelopes a part of the N atom), with the region having a marginally larger distribution nearer the N atom (Fig. 9(a)–(c)). This suggests that the B–N bond is not

completely covalent – it is slightly ionic in character. In the complete C–BN heterostructure (Fig. 9(b) and (c)), the electrons at a C atom with 2 neighbouring C atoms and a N atom (marked by a black dotted box in Fig. 9(b)) have a larger localization region between any C–C pair than between the C–N pair. Similarly, the electrons at a N atom with a neighbouring B atom and 2 C atoms (marked by a red dotted box in Fig. 9(b)) have a larger localization region between the C–N pair. This implies that electrons are more localized between a C–N pair than a B–N pair or a C–C pair, *i.e.* [C–N] > [B–N]/[C–C]. 2 two-dimensional slices of Fig. 9(c) are taken, and the electron localization landscape is drawn in Fig. 9(d); the asymmetry of the localization region presented in Fig. 9(a)–(c) is also apparent in Fig. 9(d) whereby the value of the ELF is larger around the N atom (and C atom) than around



Fig. 9 Electron localization landscape of [N-terminated; (B, N) = (top, fcc)] flake/heterostructure. Top views of (a) BN flake, (b) C–BN heterostructure, and (c) C–BN heterostructure with Cu substrate. The dotted boxes in (b) mark the neighbouring region around the N and C atoms, which is then described in Section 6. 2D slices along two planes in (c) are shown, and the landscape presented in (d). The insets include stick-and-ball schematics of the atoms. Atoms in green are B, grey are N, and brown are C.



Fig. 10 Electron localization landscape of [B-terminated; (B, N) = (fcc, top)] heterostructure. Top views of (a) BN flake, (b) C-BN heterostructure, and (c) C-BN heterostructure with the Cu substrate. The dotted boxes in (b) mark the neighbouring region around the B and C atoms, which is then described in Section 6. 2D slices along two planes in (c) are shown, and the landscape presented in (d). The insets include stick-and-ball schematics of the atoms. Atoms in green are B, grey are N, and brown are C.

the B atom. In general, the localization region between a C–C pair is much more symmetrical than between a pair of different species.

Akin to the N-terminated flake/heterostructure, in the B-terminated case (Fig. 10(a)-(c)), the localization region of isovalue 0.82 is asymmetrical about the center point between the

B–N pairs, and skewed slightly towards the N atom. However in the complete C–BN heterostructure (Fig. 10(b) and (c)), the electrons at a C atom with 2 neighbouring C atoms and a B atom (marked by a black dotted box in Fig. 10(b)) have a larger localization domain between the C–B pair than between any C–C pair. The electrons at a B atom with a neighbouring N atom

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and 2 C atoms (marked by a red dotted box in Fig. 10(b)) have a larger localization region between the C–B pair than between the B–N pair. Therefore electron localization is relatively weak in the C–B pair than in the C–C/B–N pair. The 2D electron localization landscape in the B-terminated heterostructure

(Fig. 10(d)) describes a similar chemical topology to that of the N-terminated case, with the value of ELF larger around the N atom (and C atom) than around the B atom.

The second tool is the Laplacian of the electron density. Mathematically, the Laplacian operator is a second derivative



Fig. 11 Negative Laplacian plots of (a), (b) [N-terminated; (B, N) = (top, fcc)] BN flake, (c), (d) [N-terminated; (B, N) = (top, fcc)] C-BN heterostructure, (e), (f) [B-terminated; (B, N) = (fcc, top)] BN flake, and (g), (h) [B-terminated; (B, N) = (fcc, top)] C-BN heterostructure. (a), (c), (e), and (g) are 3D plots, while (b), (d), (f), and (h) are 2D plots.



Fig. 12 Kinetic energy density (KED), potential energy density (PED), and electronic energy density (TED) of (a) [N-terminated; (B, N) = (top, fcc)] BN flake, (b) [N-terminated; (B, N) = (top, fcc)] C–BN heterostructure, (c) [B-terminated; (B, N) = (fcc, top)] BN flake, and (d) [B-terminated; (B, N) = (fcc, top)] C–BN heterostructure. The colour bar shows the energy density in $E_{\rm h}a_0^{-3}$, whereby $E_{\rm h}$ is hartree and a_0 is Bohr radius.

or the trace of the Hessian of a function; it denotes the local minimum/maximum, or in other words, the saddle point of that function. Both minimum and maximum points are critical points at which the first derivatives of the function become zero. In the context of chemical topology, the differential operator reproduces the spherical shell structure of isolated atoms by alternating shells of charge concentration and shells of charge depletion.^{39,57} The outermost shell of charge concentration of an atom is called the valence shell charge concentration (VSCC), and its spherical symmetry is broken when the atom bonds with another atom. Another feature in the Laplacian plot of the electron density is the nuclear critical point (NCP), which is a local maximum in electron density, and is typically located at the position of a nucleus. A zero-flux surface contains a set of Laplacian trajectories which terminate at the bond critical point (bcp) where the Laplacian equals zero.

In general, the covalency of the bonds is expressed by: (1) the form of the zero envelope of the negative Laplacian, and (2) the value of the negative Laplacian at the bcp. Fig. 11 shows the negative Laplacian plots of the N- and B-terminated BN and C-BN flakes/heterostructures, in the three-dimensional and two-dimensional view. The grey dots represent the bcp in the charge profile. There are 3 bcp in the vicinity of each B atom, suggesting that there is interaction between the N atoms. All bcp are surrounded by the zero envelope of the negative Laplacian - the bonds between the B and N atoms are predominantly covalent, though it has a slight ionic character (as shown in Fig. 9 and 10). The BCCs, and the locally maximum and minimum densities are marked in Fig. 11; the negative Laplacian values of the maxima and minima are shown in green and red respectively. The extension of the N-terminated BN flake to a C-BN heterostructure causes a significant drop of the local maximum Laplacian at the N atom from 86 to 64 e $Å^{-5}$, while it only reduces from 64 to 63 e $Å^{-5}$ in the case of the B-terminated heterostructure. This complements the observation in Tables 1 and 2 that the charge transfer induced by the C atoms in the complete C-BN heterostructure is more significant in the N-terminated case (0.50 e per atom versus -0.28 e per atom).

Fig. 12 compares the kinetic energy density, potential energy density, and electronic energy density at one of the vertices of each flake/heterostructure. This particular region is selected to feature the chemical topology of the different types of bond, namely B–N and C–B/C–N bonds. The electronic energy density plots complement the negative Laplacian plots (Fig. 11); it is more negative if the bond has a greater covalent character. The energy density between the B and N atoms in the flakes/ heterostructures (N- and B-terminated, BN and C–BN) is dark-blue-to-blue on the colour bar, which corresponds to approximately $-0.01 E_h a_0^{-3}$, whereby E_h is hartree and a_0 is Bohr radius. Comparatively, the energy density between the C and B/N atoms is light blue ($\sim -0.03 E_h a_0^{-3}$). Therefore, the B–N bonds are less covalent than C–B/N bonds in all configurations, regardless of the type.

7. Summary

Graphene and hexagonal boron nitride have vastly divergent electronic properties. By integrating them in a controlled fashion to form complex hybrid heterostructures in electronic devices, these properties can be tailored to suit different applications. In this study, first-principles calculations with density functional theory are performed to investigate the growth, electronic properties, and chemical topology of grapheneboron nitride lateral heterostructures. The energetics (such as formation energy, edge excess energy, binding energy), geometry (C–N/C–B bond length, flake–substrate distance), number of charges, and electric dipole moment of each system in every phase of its growth are computed and contrasted to chart their change with the growth of the heterostructure. These are summarized as follows:

(1) Growth: the growth of C atoms from either the N- or B-terminated triangular heterostructure is more energetically preferential at the vertices as compared to at the edges. Despite a small lattice mismatch between B/N and C, the structural stability of the heterostructure changes with its growth. The substrate reduces the stability of the heterostructure. In the initial growth phase, the binding energy of the N-terminated heterostructure decreases with the increase in number of C atoms. On the other hand, the converse is observed in the B-terminated heterostructure. However, in their complete C–BN lateral configurations, the binding energy is lower than that in its initial growth phase.

(2) Electronic properties: the heterostructures are metallic, likely due to charge transfer effects from the Cu(111) substrate. C atoms have a larger effect on the electronic properties of the B-terminated heterostructure.

(3) Chemical topology: the strong B–N bonds have been shown to be slightly ionic in character from the electron localization landscape and analyses of negative Laplacian plots using QTAIM. Moreover, the B–N bonds are less covalent than C–B/C–N bonds in all configurations.

Conflict of interest

The authors declare no competing financial interest.

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