Synthesis of hexagonal boron nitride heterostructures for 2D van der Waals electronics

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Among two dimensional (2D) van der Waals (vdW) layered materials such as graphene, which is used like a metal, and transition metal chalcogenides (TMdCs), which are used as semiconductors and metals, hexagonal boron nitride (hBN), which is used as an insulator, is ubiquitous as a building block to construct 2D vdW electronics for versatile tunneling devices. Monolayer and few-layer hBN films have been prepared with flake sizes of a few hundred micrometer via mechanical exfoliation and transfer methods. Another approach used to synthesize hBN films on a large scale is chemical vapor deposition (CVD). Although the single-crystal film growth of hBN on the wafer scale is the key to realizing realistic electronic applications, the various functionalities of hBN for 2D electronics are mostly limited to the microscale. Here, we review the recent progress for the large-area synthesis of hBN and other related vdW heterostructures via CVD, and the artificial construction of vdW heterostructures and 2D vdW electronics based on hBN, in terms of charge fluctuations, passivation, gate dielectrics, tunneling, Coulombic interactions, and contact resistances. The challenges and future perspectives for practical applications are also addressed.

1. Introduction

Two dimensional (2D) layered materials formed via strong covalent bonds within an individual layer and weak van der Waals (vdW) interactions between the layers can adopt various intriguing electronic structures depending on their chemical composition, with examples including graphene (metal),

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transition metal dichalcogenides (TMDCs: semiconductor/metal), and hexagonal boron nitride (hBN: insulator). 40–49 2D materials often have exotic physical and chemical properties and parameters, that are not easily observed or achieved in bulk materials, including extremely high carrier mobility, strong exciton binding energies, unusual thermal conductivity, metal–insulator phase engineering, superconductivity, giant magnetoresistance, charge density waves, strong spin–orbit coupling, Weyl semimetal properties, topological insulator properties, valleytronics, excitonics, plasmonics, polaritonics, plasmo-excitonics, defects and interface engineering. 5–23 In particular, when they are stacked together like Lego blocks to form 2D vdW heterostructures, synergetic effects lead to the formation of unprecedented new functional materials, such as atomic tunneling devices and high-performance/flexible/transparent electronics. 24–39

Among the vdW 2D materials, hBN consists of alternating boron and nitrogen atoms in a hexagonal layer and has no bonds hanging between the layers. 3 It is an insulator with a band gap of ~ 6 eV, which enables it to be extensively used as a building block for the construction of 2D vdW heterostructures and superb electronic devices. 40,41 As shown in Fig. 1, a hBN layer plays various roles in 2D vdW electronics, as a substrate for charge fluctuation reduction, 40,42–45 a passivation layer, 46–49 a gate dielectric layer, 50–53 a tunnel barrier for electronics 54–57 and optoelectronics, 58–60 a spacer layers for modulating Coulombic interactions, 61–64 and as a buffer layer for reducing metal contract resistance. 65,66 Furthermore, as a substrate and capping layer, it enables the intrinsic physical properties of 2D materials, such as the quantum confinement effect and Hofstadter’s butterfly to be observed. 67,68

To prepare a hBN layer for use in 2D vdW heterostructures, two methods, mechanical exfoliation and chemical vapor deposition (CVD), are commonly employed. 40,69,70 Mechanical exfoliation via ‘scotch tape’ involves peeling off a few layers of flakes from a hBN single-crystal grown from a bulk material using a metal solvent system. 71–76 Consequently, high quality hBN flakes can be obtained in this way. However, the size of the hBN fragments is limited to a few tens of micrometers, restricting the realization of large-area 2D vdW electronics. 40,52 Meanwhile, the CVD approach provides an opportunity to achieve wafer-scale hBN films, but the synthesis of a single-crystal hBN film still remains elusive, let alone high quality transfer at the wafer-scale. 77 To accomplish 2D vdW heterostructures, artificial transfer or direct growth via CVD has been utilized. 52,78 While artificial transfer often allows a stacking sequence of 2D vdW heterostructures, the direct growth of 2D materials on hBN is relatively difficult due to a lack of appropriate layer-by-layer growth techniques. Direct growth is the most promising way to achieve a well-defined stacking order, such as “AA or AB” at the wafer-scale scale, therefore requiring further research in the near future. While the growth of graphene and transition metal dichalcogenides and related techniques have been reviewed elsewhere, 2,79–84 a comprehensive review on the construction of 2D vdW heterostructures in terms of hBN has not been reported so far.

Dielectric materials have been improved in terms of gate dielectrics, tunnel barriers, passivation layers and so on to achieve various device functionalities for use in electronics. In device manufacturing, controllability of the thickness of a material to the atomic level, ultrafast surface morphology and defect-free dielectrics are of high importance, because such factors critically determine the device performances on the ultraminimized scale. Such issues become more serious in particular for 2D vdW electronics, at the atomic level of thickness, because the physical properties of 2D materials are easily affected by neighboring layers in vdW heterostructures. In recent emerging 2D vdW electronics, hBN has proven to be an ideal 2D dielectric material, thanks to its unique features, including no hanging bonds, an atomically flat surface, and atomic layer controllability. Therefore, as a key player in 2D vdW electronics, a comprehensive review regarding the various aspects of hBN functionalities is required in order to explore potential applications for this material.

This review consists of four section, including the introduction. In the following section, Section 2, we introduce the preparation

**Fig. 1** Applications of hBN layer for 2D vdW electronics.
method for the construction of a 2D vdW heterostructure based on hBN via CVD and artificial transfer. The surface-mediated and precipitated growth of wafer-scale monolayer and multilayer hBN films is first introduced. The construction of in-plane and vertical 2D vdW heterostructures with other 2D materials, such as graphene, MoS$_2$, and ZrS$_2$, on either mechanically-exfoliated or CVD-grown hBN is also addressed. In-plane heterostructures, for example, the growth of hBN from the edge of graphene, are possible to create via direct growth, not by artificial transfer. The artificial transfer method, used to engineer the 2D stacking sequence in 2D vdW heterostructures, is further reviewed. In Section 3, the diverse range of electronic properties of 2D vdW heterostructures based on hBN, including charge fluctuations, passivation, gate dielectrics, tunneling, Coulombic interactions, and contact resistances are discussed. Finally, in Section 4, a summary is given and perspectives detailing the realization of the applications of 2D vdW electronics is addressed.

2. Preparation of 2D van der Waals heterostructures

2.1. Synthesis of wafer-scale hBN films via CVD

Two representative methods, CVD and molecular beam epitaxy (MBE), have been proposed to obtain a wafer-scale hBN film. The CVD approach has some advantages, including low cost, high throughput, productivity, and scalability for the wafer-scale hBN film, in contrasted with the MBE approach. We focus on the CVD method for the synthesis of a hBN film for real applications. The formation of both monolayer and multilayer hBN films is essential, for several purposes, for example, monolayer hBN is used as a filter for hydrogen isotopes and for the reduction of the Schottky barrier height between an electrode and channel material, and multilayer hBN is used as a dielectric layer and passivation layer for other semiconducting 2D materials. To control the thickness of a hBN film using a CVD approach, one primary concern is how to determine the solubility of the boron and nitrogen atoms in the substrate prior to further growth. For example, a monolayer hBN film can be grown on a Cu substrate by taking advantage of the limited solubility of boron and nitrogen atoms, whereas a multilayer hBN film can be grown on an iron substrate by taking advantage of the finite solid solubility of boron and nitrogen atoms.

2.1.1. Monolayer hBN films. Monolayer hBN films have been synthesized on various substrates, such as single crystalline metals of Ni(111), Rh(111), Cu(111), or Ru(0001) or polycrystalline metals of Cu, Pt, and Au foils/films via CVD. The negligible boron and nitrogen solubility in the aforementioned substrates at the growth temperature leads to the exclusive growth of a monolayer hBN film on the surface of the growth substrate. This review focuses on the growth of hBN on polycrystalline metal foils or films for use in commercial applications. The growth of hBN films on single-crystal metal substrates has been well described elsewhere. A representative CVD setup for the growth of monolayer hBN on Cu foil is illustrated in Fig. 2a. To vaporize the solid ammonia borane (BNH$_3$) used as the BN precursor, the temperature is elevated to around 100 °C with a heating belt. The ammonia borane is decomposed to hydrogen, borazine, and aminoborane in the vapor phase at high temperature. Several issues still occur, for example, less controllability and unwanted by-products such as onion-like BN particles. To remove the onion-like BN particles, a CVD system has been suggested whereby a filter sheet is installed at the inlet line. Low-pressure CVD allows for the diffusion of the precursor into the furnace without the use of a carrier gas. It is also possible to supply the precursor under atmospheric pressure using a carrier gas. The growth of hBN is typically executed at around 1000 °C. The triangular hBN domain at the early growth stage and the corresponding illustrative edge structure are presented in Fig. 2b and c. In theory, the edge energy in a triangular hBN domain terminated by nitrogen atoms is lower than that terminated by boron atoms, resulting in the formation of an N-terminated triangular hBN domain. The scanning electron microscopy (SEM) images in Fig. 2d–h show the as-grown hBN on Cu foil as a function of growth time, at 10, 15, 40, 60 and 120 min. At the initial stage (Fig. 2d), the grown of a triangular hBN domain is observed, followed by the extension of hBN from one of the triangular edges to form an asymmetric diamond-shaped hBN domain. Asymmetric diamond-, hexagonal-, truncated-, and circular-shaped hBN domains are also observed, attributed to the different growth kinetics involved, such as the diffusivity of adatoms of BN radicals. The hBN domains are further synthesized across the Cu grain boundaries, as indicated by the white-dashed line in Fig. 2e, implying that hBN growth is governed by a surface-mediated process. With a prolonged growth time, the formation of a monolayer hBN film is completed by a merging together of the hBN domains (Fig. 2f). The hBN wrinkles, indicated by the white arrow in Fig. 2f, are visible, which are thought to be caused by the thermal expansion coefficient difference between hBN and Cu. Overlayered multilayer hBN domains on the top of the monolayer hBN film are partially visible upon further growth (Fig. 2g and h). The magnified SEM image of the red-dashed box in Fig. 2h shows the presence of multilayer triangular hBN domains (Fig. 2i), revealing that monolayer hBN growth is presumably first governed by the Frank van der Merwe model, due to the strong interaction between adatoms and growth substrate and then converted into Stranski–Krastanov growth for multilayer grains.

In addition, monolayer hBN films have been synthesized on Pt foil, using an approach similar to that used for Cu foil. Since Pt foil is not easily etched away during the transfer process, bubble transfer can be employed. Furthermore, Pt foil can be reused repeatedly for the re-growth of hBN films. To conduct bubble transfer, poly(methyl methacrylate) (PMMA) is first spun on the hBN/Pt foil as a supporting layer, followed by delamination with hydrogen bubbles generated between PMMA/hBN and the Pt foil at the anode in aqueous NaOH solution (Fig. 2j). The detached PMMA/hBN film is washed with fresh water to remove any impurities and then transferred onto the target substrate. The supporting layer is removed with acetone.
The photograph and SEM image show a centimeter-scale hBN monolayer film on the target substrate (Fig. 2k and l). Furthermore, Au foils have also been used to grow hBN monolayer films. Until now, the growth of hBN monolayer films on Cu foil and transfer of up to 25 inches has been achieved. The remaining issues so far for the synthesis of monolayer hBN films are (1) the growth of single-crystal monolayer hBN films, (2) wrinkle-free growth, (3) dry transfer without damage or defects, (4) direct growth on a dielectric substrate without transfer, and (5) ensuring reproducibility of the growth.

2.1.2. Multilayer hBN films. The key idea for the growth of multilayer hBN film is the use of a finite solubility of boron and nitrogen in substrate. Iron is predominantly used as a substrate due to a finite solubility of nitrogen (\( \sim 8 \) at%) at 1000 °C and the formation of FeB\(_x\) \((x = 1 \text{ and } 2)\) compound at growth temperature. Therefore, the B and N atoms are preferentially segregated out of the iron substrate during the cooling process to form a multilayer hBN film. The sandwich structure of the Fe film/B, N source/Ni substrate illustrates the configuration required for the growth of a multilayer hBN film under vacuum annealing (Fig. 3a). The boron and nitrogen atoms evaporate onto the Ni substrate, followed by the evaporation of the Fe film. With the elevation of the temperature under vacuum, the boron and nitrogen atoms diffuse into the Fe film. During the cooling process, the B and N atoms are co-segregated to form a multilayer hBN film. The thickness of the hBN film is controlled by either the thickness of B/N or the Fe film. The optical image of the transferred multilayer hBN film on the SiO\(_2\)/Si substrate shows the growth of a large surface area hBN film (Fig. 3b). The inset of Fig. 3b shows the high transparency of the hBN film transferred onto a quartz substrate at the centimeter scale. Both the distinct N and B core level spectra show the stoichiometry of B and N to be 1.06 : 1 and the characteristic \( E_{2g} \) phonon mode near 1369 cm\(^{-1}\) in the Raman spectrum reveals the successful growth of the hBN film (Fig. 3c and d). The transmission electron microscope (TEM) image in Fig. 3e and the corresponding fast Fourier transform pattern prove that the hBN film has a hexagonal structure and a lattice constant of 0.25 nm. The layer distance in the multilayer hBN film is 0.33 nm at the folded hBN edge, which is in good agreement with previous observations (Fig. 3f). The electrical conductivity is almost zero, attributed to the insulating nature of hBN (Fig. 3g).

Another approach is the direct growth of a multilayer hBN film on Fe foil (Fig. 3h). Liquid borazine is supplied into the furnace with a bubbler system. The multilayer hBN film grows...
at around 1100 °C and solubilizes B and N into the Fe foil, followed by cooling of the furnace with a controlled cooling rate of 5 °C min⁻¹ until 700 °C is reached. The photographs of the as-grown and transferred hBN on SiO₂/Si substrate show the successful growth of a centimeter-scale hBN film (Fig. 3i). The distinct wrinkles indicated by white lines can be clearly observed in the SEM image (Fig. 3j). Since the wrinkles have an impact on the reliability of electronic devices when hBN is used as a dielectric layer, another approach required is to investigate forming a wrinkle-free hBN film. The clear characteristic peaks at 5.77 and 5.46 eV assigned to the excitons of hBN in the cathodoluminescence (CL) spectrum demonstrate that the hBN is of high quality (Fig. 3k). Further characterization, using TEM, Raman and XPS spectroscopies, and dielectric properties, support that the quality of the multilayer hBN film is similar to that of single-crystal hBN. Unfortunately, the thickness of the multilayer hBN film is not controlled precisely owing to the different precipitation rate from the diverse grain in the polycrystalline Fe foil and the grain boundaries between the Fe grains. Other works have also suggested the growth of multilayer hBN films on single crystal Ni(111) or Ru(0001) films using solid epitaxy growth, followed by thermal annealing to induce the recrystallization of an amorphous hBN film along the underlying lattice orientation.⁷⁰,¹¹¹ A single-crystal sapphire substrate has been used for the direct growth of a multilayer hBN film on the wafer scale at 1400 °C, demonstrating that hBN films can be epitaxially grown on single-crystal substrates.¹¹² Nevertheless, the thickness of the hBN film is not precisely controlled. The remaining issues so far in the synthesis of multilayer hBN films are (1) the growth of a wrinkle-free and single-crystal multilayer hBN film and (2) control of the thickness and uniformity of the hBN film.

2.2. Synthesis of a wafer-scale vdW 2D-hBN heterostructure via CVD

The synthesis of vertical and lateral 2D heterostructures on the respective basal plane and at the edge of the hBN layer has been developed by combining the growth techniques of other 2D materials, such as graphene and TMDCs. To grow 2D heterostructures, several issues prior to growth should be considered; (1) the hBN substrate should not be etched away by the precursor to allow the further growth of the 2D material, (2) the chemical reaction between the underlying substrate of the hBN film and precursors should prevent unwanted metal alloy
or compound formations, such as sulfide or selenide compounds, and (3) the precursors should effectively decompose to grow 2D materials on the insulating hBN substrate. In this section, the growth of graphene and TMdcS on a hBN substrate or at the edge of a hBN layer is reviewed.

2.2.1. An epitaxial vertical 2D/hBN heterostructure. To epitaxially synthesize a vertical 2D/hBN vdW heterostructure by CVD, single-crystal hBN flakes prepared by mechanical exfoliation are used as a growth substrate at the initial stage. To effectively decompose the carbon precursors for the growth of graphene on the insulating hBN substrate, a gaseous catalyst is used. The epitaxial growth of graphene on hBN (Gr/hBN) with a gaseous silane catalyst for the decomposition of acetylene gas is illustrated in Fig. 4a. The growth rate of graphene in the presence of silane gas (~400 nm min⁻¹) at 1280 °C is four times higher than that in germane gas (~50 nm min⁻¹), indicating that silane is more effective in decomposing the carbon precursor (Fig. 4b). The atomic force microscopy (AFM) shows that the hexagonal graphene domains grew well (Fig. 4c).

To evaluate the presence of the moiré pattern, domains 1 and 2 in Fig. 4c were further measured using high resolution AFM (Fig. 4d and e). While the moiré pattern in domain 1 is clearly

Fig. 4 Synthesis of a vertical 2D vdW heterostructure on single-crystal hBN flakes by CVD. (a) Schematic illustration of the gaseous catalyst (SiH₄)-assisted CVD process. (b) Growth rates of Gr/hBN with silane (black) and germane (red) with gaseous catalysts and no catalyst (green) at 1280 °C. (c) Topography images of two graphene domains grown on a hBN surface. The white line indicates a wrinkle on the hBN surface; the scale bar is 2 μm. (d and e) Magnified views of the red and blue boxes in (c). (f) Schematic illustration of epitaxial graphene growth on a hBN surface by PECVD. (g) AFM image of as-grown graphene on hBN; the scale bar is 200 nm. (h) AFM image of as-grown graphene on hBN; the scale bar is 100 nm. (i) High-pass-filtered inverse FFT in the dashed square in (h) with the height profile shown along the dashed line. Reprinted with permission from ref. 113. Copyright 2013 Springer Nature. (j) The CVD setup for single- and few-layer MoS₂ growth on hBN/SiO₂/Si. (k) Optical image of a typical MoS₂ island on hBN/SiO₂/Si. (l) PL spectra of as-grown single- and few-layer MoS₂ on hBN/SiO₂/Si. (m) A typical SAED pattern of MoS₂ grown on hBN; MoS₂ (green) and hBN (purple). (n) A histogram of the relative rotation angle of single-layer MoS₂ on hBN. Reprinted with permission from ref. 114. Copyright 2015 American Chemical Society. (p) SEM image of triangular WS₂ domains grown on hBN. (q) Low energy electron microscope (LEEM) image of an as-grown WS₂ crystal. (r) LEED pattern measured at position 1 in (q) with an electron energy of 50 eV. Reprinted with permission from ref. 115. Copyright 2014 American Chemical Society. (s) SEM image of triangular ZrS₂ domains grown on hBN. (t) A typical SAED pattern of ZrS₂ grown on hBN; ZrS₂ (red) and hBN (white). Reprinted with permission from ref. 116. Copyright 2015 American Chemical Society.
observed with a wavelength of \( \sim 13.9 \text{ nm} \) at a zero rotation angle, domain 2 is not observed due to the presence of hBN wrinkles. This implies that a flat hBN substrate is important to lead epitaxial growth. In this work, around 93.1% of the graphene domains are well-aligned on hBN as in domain 1, implying that graphene predominantly undergoes epitaxial growth on the hBN substrate.

On the other hand, plasma-enhanced CVD (PECVD) was also employed to effectively decompose methane gas at a lower temperature of \( \sim 500 \text{ °C} \).\(^{113}\) The growth of Gr/hBN is illustrated in Fig. 4f. The AFM image shows the well-aligned hexagonal graphene domains along a specific direction (Fig. 4g). The coalesced graphene domain region to characterize the grain boundary was further analyzed with AFM (Fig. 4h). The moiré pattern was clearly observed without any noticeable grain boundary. To analyze the periodicity of the moiré pattern, the high-pass-filtered inverse FFT in the white-dashed box in Fig. 4h was obtained. The height profile along the yellow-dashed line indicates that the periodicity of the moiré pattern is around \( \sim 15 \text{ nm} \) (Fig. 4i), implying that the graphene domains are well aligned with the underlying hBN lattice, free from a grain boundary when merged.

The growth of TMdCs such as MoS\(_2\), WS\(_2\), and ZrS\(_2\) on hBN has been reported.\(^{114-116}\) The typical CVD setup for the growth of MoS\(_2\) is illustrated in Fig. 4j.\(^{114}\) Two heating zones (zone 1: \( \sim 500 \text{ °C} \) and zone 2: \( 800 \text{ °C} \)) consist of evaporating solid phases of S and Mo precursors for the growth, respectively. The schematic illustration of an as-grown monolayer MoS\(_2\) on an hBN substrate and the corresponding optical image of the sample are presented in Fig. 4k and 1. Photoluminescence (PL) spectroscopy was employed to characterize the optical band gap of the as-grown monolayer MoS\(_2\) on hBN (Fig. 4m). The optical band gap (1.89 eV) and full-width at half maximum (FWHM) (40 meV) of the PL peak for the as-grown MoS\(_2\) on hBN substrate are quite similar to those of a suspended monolayer MoS\(_2\) prepared by mechanical exfoliation, implying that MoS\(_2\) grown on an hBN substrate is electrically less perturbed.\(^{114}\) The lattice orientation of MoS\(_2\) on hBN was further characterized from the electron diffraction pattern in the TEM. One of the selective area electron diffraction (SAED) patterns show that the rotation angle of the six-fold-symmetric diffraction spots of MoS\(_2\) with respect to those of hBN, respectively, are present in Fig. 4n and o. The green and purple hexagons show the six-fold-symmetric diffraction spots of respective MoS\(_2\) and hBN with a relative rotation angle of \( 9^\circ \) (Fig. 4n). The histogram for counts shows that 10 out of 22 monolayer MoS\(_2\) domains grown on the hBN substrate have a relative rotation angle within \( 6^\circ \) (Fig. 4o), which can be attributed to the preferred vdW epitaxy.\(^{119}\) Furthermore, with diluted growth condition, two highly dominant relative orientations of 0° and 60° predominantly grow on the hBN substrate, indicating that vdW epitaxy occurs in a commensurate manner despite the high lattice mismatch (> 20%) between hBN and MoS\(_2\).

In addition, WS\(_2\) and ZrS\(_2\) domains on hBN have been synthesized using a similar method. The difference with the MoS\(_2\) is in the growth temperatures used for the evaporation of the precursors and growth of WS\(_2\) or ZrS\(_2\). The triangular and inverted triangular WS\(_2\) domains relatively rotated by 60° are clearly observed (Fig. 4p and q), indicating that the hBN substrate restricts the lattice orientation of WS\(_2\) domains.\(^{115}\) The two hexagonal patterns with 3-fold symmetry from hBN and WS\(_2\) in the low-energy electron diffraction (LEED) from the white-dotted circle 1 in Fig. 4q are perfectly coincident (Fig. 4r), indicating that the lattice orientation of the WS\(_2\) domains is confined by the underlying hBN substrates. On the other hand, the hexagonal ZrS\(_2\) domains on the hBN substrate preferentially grow along a specific direction within a small rotation angle of 3° (Fig. 4s).\(^{116}\) The TEM observations and the corresponding SAED patterns show that the d-spacings of the (10–10) and (11–20) planes of ZrS\(_2\) and hBN are 3.2 and 1.8 Å for ZrS\(_2\), and 2.2 and 1.2 Å for hBN, respectively (Fig. 4t and u). The relative rotation angle between the two six-fold-symmetric hexagonal spots is around 1°, indicating that vdW epitaxy is preferred. The statistics for the relative orientation reveal that a stacking angle of 0° is preferred for ZrS\(_2\) is (not shown here).\(^{116}\) The remaining issues for the growth of a vertical 2D/hBN heterostructure film are (1) the preparation of a wafer-scale single-crystal hBN substrate, (2) the control of the growth kinetics for vdW epitaxy, and (3) the development of a layer-by-layer growth technique. Furthermore, the control of the lattice orientation of triangular-shaped TMdC domains with identical directions is critical for growing single-crystal vertical TMdCs/hBN heterostructures.

### 2.2.2. A wafer-scale vertical 2D/hBN heterostructure

To realize the growth of a vertical 2D/hBN heterostructure on the wafer-scale, a large surface area poly-crystalline hBN substrate has been prepared by CVD. Since a monolayer hBN film can be easily etched away by hydrogen, carbon dioxide, and oxygen, a special design for the overlayer growth is necessary. A two-step growth route for Gr/hBN/Cu foil has been reported as an example (Fig. 5a).\(^{120}\) The hBN film was first grown on Cu foil with ammonia borane, followed by the growth of graphene under a nickelocene atmosphere. Nickelocene (C\(_{10}\)H\(_{12}\)Ni), as a carbon precursor, was introduced to prevent the etching of the hBN film during the growth of the graphene. Moreover, the Ni atoms in nickelocene promote the decomposition of hydrocarbons, resulting in an increase in the growth rate compared to that using no-catalyst or benzoic acid.\(^{122}\) The TEM and corresponding SAED images show that the six-fold-symmetric hexagonal spots are almost aligned with the hBN lattice, implying that graphene is grown by vdW epitaxy in the local region (Fig. 5b and c). Another approach has been reported to construct Gr/hBN, using a co-segregation method.\(^{123}\) A sandwich structure of C-doped Ni film/B, N source/Ni film was prepared using an electron beam evaporator (Fig. 5d). During the thermal annealing process, the carbon firstly diffused out from the C-doped Ni film to form graphene, followed by the segregation of B and N atoms via inter-diffusion across the C-doped Ni film, eventually leading to the growth of a vertical Gr/hBN heterostructure. Both the finite solubility of N/C and formation of NiB\(_x\) \((x = 1, 2, 3)\) compounds in Ni permit the co-segregation out of the Ni film. The stacking angle between the graphene and hBN was further characterized from the SAED patterns (Fig. 5e and f). While the moiré pattern with a
wavelength (λ) of 1.28 nm corresponding to the relative rotation angle of 11° in one region is observed, only one set of six-fold-symmetric hexagonal spots without a moiré pattern at the other region is visible with a hexagonal lattice spacing of 0.25 nm. This indicates that the stacking order between graphene and hBN is random using this approach.

Compared to the vertical Gr/hBN heterostructure, the growth of the vertical TMdCs/hBN heterostructure is more restricted due to the chemical reaction between the chalcogen (S, Se, Te) and metal substrate used for the hBN growth. For example, Cu, Ni, or Pt substrates easily react with sulfur atoms to form copper, platinum, or nickel sulfides, respectively. Therefore, careful choice of the growth substrate is required. Until now, sulfur-resistant Ni–Ga alloy and Au foil substrates have been used for the growth of vertical MoS2/hBN heterostructures.95,121 The growth of a MoS2/hBN stack by CVD is illustrated in Fig. 5g–i. 121 The high formation energy of the Ni–Ga intermetallic compound (Ni5Ga3) allows for the resistance of the sulfurization. A Ni–Ga alloy on Mo foil is firstly prepared using a thermal annealing process. The hBN film with ammonia borane is synthesized on the prepared substrate, followed by the growth of MoS2 under a H2S atmosphere. The Mo atoms are supplied from the bottom of the Mo foil. Triangular- or hexagonal-shaped MoS2 flakes on hBN film are
clearly observed in the SEM image (Fig. 5j). The distinct lattice fringes between the hBN and MoS$_2$/hBN region are displayed in the TEM image (Fig. 5k). The d-spacings of the (11–20) and (10–10) planes of MoS$_2$ were measured to be 0.16 and 0.27 nm, respectively (shown in the bottom right of the inset). The two sets of hexagonal spots rotated by 30° corresponding to the SAED pattern shown in blue (MoS$_2$) and green (hBN) reveal that MoS$_2$ is not epitaxially grown on hBN.

Meanwhile, Au foil has been employed to grow a MoS$_2$/hBN heterostructure. Ammonia borane, used as a precursor, was introduced to synthesize an hBN film over Au foil at 1030 °C, followed by the growth of MoS$_2$ on top of the hBN film with the evaporation of MoO$_2$ and sulfur powder (Fig. 5l). The SEM image of the as-grown sample presents the formation of MoS$_2$ on hBN/Au foil (Fig. 5m). The annual dark-field (ADF)-scanning tunneling electron microscopy (STEM) image of the edge of a MoS$_2$ domain on hBN shows no obvious defects in the MoS$_2$ domain, suggesting high-quality (Fig. 5n). One of the SAED images shows that the hexagonal lattice of the MoS$_2$ flake is rotated by 9° relative to that of hBN (Fig. 5o). The statistics for the rotation angle from 12 different regions indicate that there is no preferred rotation angle (Fig. 5p), which is distinct result with MoS$_2$ grown on single-crystal hBN. The challenging issues that remain for vertical 2D hBN heterostructures are (1) the synthesis of a single-crystal hBN substrate on the wafer-scale, (2) the development of 2D/hBN vdW epitaxy growth, (3) the search for a new substrate with a high resistance for chalcogens, and (4) the investigation of liquid or gas phases precursors for transition metals and chalcogens.

2.2.3. Wafer-scale in-plane 2D–hBN heterostructures. An in-plane 2D–hBN heterostructure was initiated from the growth of an in-plane graphene–hBN (Gr–hBN) heterostructure via CVD, where hBN flakes on Cu foil were first synthesized and subsequently graphene flakes were grown at the edge of the hBN flakes. Using an advanced growth technique, an in-plane Gr–hBN–Gr heterostructure is demonstrated by alternatively introducing the precursor ethylene and borazine gases every 50 s (Fig. 6a and b). The contrast in the SEM image differentiates the graphene strips from the hBN strips grown on Ru(0001) (Fig. 6c–e). This result implies that in-plane heteroepitaxy is preferred at the edge of each material. In addition, an in-plane Gr–hBN heterostructure was also realized by the patterned growth of graphene at the etched region between the hBN regions (Fig. 6f). The as-grown hBN film on Cu/Ni foil with ammonia borane is selectively etched away using laser-cut masks for the various patterns, followed by graphene growth in the etched region supplying the methane at 1000 °C. This allows for the formation of an owl-patterned in-plane Gr–hBN heterostructure (Fig. 6g). The ADF-STEM image clearly shows the border between the hBN and graphene regions (Fig. 6h). Furthermore, the EELS mapping image of the boron atoms shows the sharp interface between the hBN and graphene regions (Fig. 6i). However, the two sets of hexagonal spots from the hBN and graphene lattices at the junction region in the FFT pattern are randomly rotated (not shown here), indicating that in-plane epitaxy growth does not take place.

Meanwhile, the catalytic conversion of hBN to graphene has been suggested rather than etching and selective growth. The reaction of BN (hBN) + 3CH$_4$ → 3C (graphene) + 2HB$_3$ + 2NH$_3$ is a thermodynamically endothermic process with an enthalpy (ΔH) of 810.63 kJ mol$^{-1}$, indicating that the high activation energy barrier for the conversion should be overcome for the forward reaction to proceed. To overcome the activation energy, a catalytic Pt substrate is utilized. Fig. 6j illustrates the experimental procedure for the catalytic conversion to form an in-plane Gr–hBN heterostructure. The hBN film grown by CVD is transferred onto the patterned Pt/SiO$_2$ substrate, followed by the introduction of methane at 1000 °C for the conversion of hBN to graphene on the Pt surface. The optical image and the corresponding Raman mapping image for the 2D peak near 2700 cm$^{-1}$ (yellow-dashed box) clearly demonstrate the formation of an in-plane Gr–hBN heterostructure (Fig. 6k and l). It is noted that while the conversion on the Cu substrate is not preferred, a minimal and slower reaction is found on the Ru substrate. This illustrates that better understanding of the role of metal substrates is further needed in the near future.

In addition, the direct growth of an in-plane hBN–MoS$_2$ heterostructure has been demonstrated. To facilitate MoS$_2$ growth at the edge of hBN, a seeding promoter was employed. Fig. 6m illustrates the synthesis of an in-plane MoS$_2$–hBN structure with the selective “sowing” of seed perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS) molecules. It is more likely that seeds are deposited on the hydrophilic SiO$_2$ substrate rather than the hBN substrate, playing the role as a promoter when MoS$_2$ is grown at the edge of hBN flakes on the substrate. The optical image of the as-grown sample and the corresponding PL mapping image of the A exciton peak of MoS$_2$ demonstrate the growth of MoS$_2$ at the edge of the hBN flakes (Fig. 6n and o). The AFM image in the inset of Fig. 6n further supports the successful growth of an in-plane hBN–MoS$_2$ heterostructure. Furthermore, the growth of graphene–MoS$_2$ and WS$_2$–MoS$_2$ heterostructures using an approach similar to this has also been demonstrated. The remaining issues for in-plane 2D–hBN heterostructures are (1) the development of in situ patterned homoepitaxial growth for a sharp heterojunction on the wafer scale and (2) exploring other in-plane 2D–hBN heterostructures. 2.3. Engineering the 2D/hBN stacking sequence by transfer Direct growth, for example by CVD, is the most promising way to form vertical 2D/hBN vdW heterostructures at the wafer scale, but it is still challenging to realize unique 2D vdW heterostructures due to the absence of a well-defined vdW epitaxial growth technique. Thus, artificial transfer has been developed as an alternative approach to study the physical properties and potential applications of 2D/hBN heterostructures. Mechanical exfoliation is typically utilized to achieve monolayer 2D materials from single-crystal bulks with weak vdW interactions between the 2D layers. One of the main
issues of mechanical exfoliation is to obtain a 2D material on the substrate as large as possible in size. Fig. 7b–f shows the modified mechanical exfoliation process: the SiO$_2$/Si substrate and graphite on the adhesive tape, the cleaning of the substrate by oxygen plasma, heat treatment ($1001^\circ$C in air), and peel-off of the graphite flakes. $^{133}$ The optical image shows that the size of the graphene ranges from $20\mu m$ to above $100\mu m$ (Fig. 7g). This modified method improves the chances of achieving larger sized graphene by more than 7 times compared to the conventional method, which is conducted with no surface and heat treatments. The key ideas behind this method include the oxygen plasma treatment for removing any adsorbates on the substrate, heat treatment for releasing the encapsulated gases between the graphite and substrate by elevating the internal pressure ($P > P_{int}$) (Fig. 7h–j). Furthermore, it was demonstrated that this approach can be applied to other 2D layered materials such as BiSr$_2$CaCu$_2$O$_{x}$.

To construct 2D/hBN vdW heterostructures, 2D materials have been stacked using transfer apparatus. $^{135}$ This consists of an XYZ-position manipulator and a heating stage for the optical microscope, allowing for the control of the stacking alignment between the 2D materials (Fig. 7k). To pick up a 2D material, a polymer block of polypropylene carbonate (PPC)/polydimethylsiloxane (PDMS)/tape on a slide was prepared (Fig. 7l and m). The surface of PDMS was treated with oxygen plasma before being coated with PPC to prevent the delamination of PPC from PDMS during the transfer process at a high temperature ($> 100^\circ$C). The temperature of the stage is important to determine whether the 2D material is “picked up” or “dropped down” (Fig. 7n). A temperature of $40^\circ$C at the stage is sufficient.
for the hBN flakes to be picked onto the PPC film, whereas a temperature of above 110 °C allows the hBN flakes to adhere onto the graphene at the bottom through strong vdW interactions, as shown in Fig. 7n(i–iii). The high temperature process, that is above the boiling point of water, helps to remove any water contamination between the hBN and graphene. It is noted that the slight tilt of the substrate by a few degrees during drop-down significantly removes the blister formation between the hBN and graphene (step iii in Fig. 7n). Furthermore, to construct a hBN/graphene/hBN heterostructure, the same process was conducted, as shown in Fig. 7n(iv–vi).

3. hBN Applications for 2D van der Waals electronics

Recent advances in information technology demand next generation electronic devices with low-power consumption, high operation speed, and ultrahigh scalability. Complementary metal-oxide-semiconductor (CMOS) technology has led to the generation of electronics so far. However, such top-down methods face various problems at the sub-10 nm scale, such as operation speed delay, Joule heating, and the miniaturization limit of the physical dimensions.19,136,137 Meanwhile, among the counterparts of the CMOS technique, vdW heterostructures based on 2D materials have been highlighted.138,139 Various combinations of heterostructures can be fabricated by vertical vdW stacking of 2D materials. This platform allows for studying the potential applications of high performance field-effect transistors (FETs), tunneling devices, and optoelectronics, in addition to the unexplored physical properties of the interlayer excitons, and Coulombic drags in the atomic layer thickness.1

Fig. 7 Artificial construction of vertical 2D/hBN vdW heterostructures. (a) Schematic diagram of a 2D vdW heterostructure. Reprinted with permission from ref. 24. Copyright 2013 Springer Nature. (b–f) Mechanical exfoliation process of graphite flakes onto a Si/SiO2 substrate; (b) SiO2/Si substrate and graphite flakes on an adhesive tape, (c) oxygen-plasma cleaning process of a SiO2/Si substrate, (d) contact between the graphite flake-decorated tape and the cleaned SiO2/Si substrate, followed by heating on a hot plate in air at 100 °C for 2 min, (e) peeling-off of the adhesive tape, and (f) exfoliated graphene/graphite flakes on a SiO2/Si substrate. (g) Optical image of graphene flakes on the substrate. (h–j) Mechanism between the graphite/support interface. (h) Removal of adsorbates by oxygen plasma. (i) Increase in pressure at the graphite-support interface (P_int) at elevated temperature (T > 100 °C), releasing the gases (P < P_int). (j) Reduction of the pressure at the interface at a reduced temperature (T < 20 °C), resulting in a tightened interface (P > P_int). Reprinted with permission from ref. 133. Copyright 2015 American Chemical Society. (k) Manipulator with slide assembly used for the construction of a 2D/hBN heterostructure. (l and m) Polymer block (PPC/PDMS/tape) on a glass slide used for the pick-up and drop-down processes. (n) Schematic illustration of the assembly of 2D heterostructures by the “picking-up” and “dropping-down” of a polymer block. (o) Optical image of a graphene/hBN stack on PPC after step-iv in (n). (p) AFM image of the black-box region in (o).
In 2D vdW transistors, fluctuation of the charge carriers during transport in channels is a bottleneck in achieving a high speed and low power operation. The carrier mobility in the thin channel layer is easily affected by substrate properties such as defects, charge traps, and roughness, and environmental factors including unwanted adsorbates from the surroundings. The use of hBN as a substrate can reduce the charge fluctuation, owing to the unique features of the ultraflat and dangling-bond-free surfaces of hBN,40,42–45,138 which will be discussed in Section 3.1. Additionally, for robust carrier transport performances and good device reliability, passivation techniques are widely used. In comparison to other oxide thin films, hBN has excellent passivation performances, even for unstable materials, thanks to its high crystallinity and good compatibility with 2D materials,46–49 which will be discussed in Section 3.2.

As a gate dielectric for 2D vdW electronics, hBN exhibits a high on/off switching ratio at the optimum thickness and robust performances for flexible substrates. Therefore, the hBN properties of it used as a promising gate dielectric material will be discussed in Section 3.3.30,50–53 For low-power and high-speed electrical switching, although tunneling devices using interlayer tunneling effects are favorable compared to conventional FETs with long channel transports, a thin and defect-free tunnel barrier is crucial for a reliable performance. In particular, to precisely control the quantum effects, the tunnel barrier thickness should be manipulated and has a good uniformity at the atomic level. With the atomic tunnel barriers, the usefulness of a thin hBN layer for tunneling FETs, magnetic tunnel junctions, tunneling memories, tunneling photoeffect properties, and tunneling light emitters will be discussed in Section 3.4.2–5 Moreover, this barrier thickness on the atomic scale is also important for modulating the Coulombic interactions. Unexplored physical phenomena based on the interlayer Coulombic interactions with a few layer hBN spacers will be discussed in Section 3.5.61–64 Few-layer hBN is also utilized for reducing Schottky barriers in metal/semiconductor contacts in 2D vdW electronics. The introduction of 1–2 layers of hBN at Schottky barrier interfaces effectively modulates the metal work function and interface properties, resulting in reduced contact resistances, which will be discussed in Section 3.6.48,66

3.1. Charge fluctuation

To realize high speed and low power consumption in 2D electronic devices, high carrier mobility in the channel layer and low contact resistance between the metal electrodes and semiconductor active layers are essential. While SiO2 dielectric layers on the Si wafer are typically used in 2D material research as substrates, the carrier mobility is critically limited by the charge fluctuation in the SiO2 layers. Amorphous SiO2 layers typically grown by the dry or wet oxidation of a Si substrate possess rough surface morphology and contain dangling bonds, charge trapping, impurities and vacancies, resulting in prominent fluctuations of transporting carriers in the 2D active channels.49,42,140–143 Meanwhile, hBN prepared by exfoliation of single-crystal flakes can prominently reduce such charge fluctuation effects due to the nature of ultra-flat and defect-free-surfaces.40,42–45,144–151

Fig. 8a–f show the comparative characteristics of charge fluctuation in graphene on SiO2 and hBN substrates measured by scanning tunnelling microscopy (STM), where the graphene flake is connected to gold electrodes for electrical contact (Fig. 8a). A histogram comparison of the height distributions for graphene on SiO2 and hBN (Fig. 8b) and each surface corrugation image (Fig. 8c and d) reveal the notable surface flatness of hBN compared to the rough SiO2 surface (Fig. 8a–d). Moreover, while the histogram of the Dirac point energy distribution of the SiO2 substrate is prominent, that for the hBN substrate is much more reduced due to decreased impurity densities (Fig. 8e and f). This charge fluctuation effect has also been intensively investigated for carrier transport properties using monolayer MoS2 transistors.43–45

A schematic of MoS2 transistors on SiO2 and hBN substrates with four-terminal electrodes is illustrated in Fig. 8g. From the gate-bias dependent mobilities at various temperatures, the Coulombic scattering parameters as a function of the carrier density and temperature were experimentally determined for each transistor (Fig. 8h). The charge trapping–detrapping process at the gate dielectrics, as a main noise source in the channel, results in the prominent suppression of the Coulombic scattering parameter. Notably, the current fluctuation of the hBN substrate at 25 K prominently decreases compared to that for the SiO2 substrate at every current level (Fig. 8i), which is attributed to a reduction in the Schottky barrier noise between the metal contact and MoS2. Moreover, hBN prohibits electron trapping to SiO2 in the MoS2 channel. Positive excess electrons in the channels of hBN (Fig. 8j) allows for an effective n-doping effect, resulting in reduced Schottky barriers (Fig. 8k).

Although hBN substrates exhibit an insightful charge fluctuation reduction performance, some issues remain elusive. The defective surface on SiO2 also affects the metal/semiconductor contact in 2D electronics so that the Schottky barrier level also fluctuates because the substrate effect determines the semiconductor properties below the metal contacts because of the thin layer thickness, likewise in the channel region. To reduce the Schottky barrier fluctuation, the usefulness of the hBN substrate has been comprehensively investigated.152 The carrier transport properties and reliability of the thin 2D channels are also seriously affected by environmental factors, such as adsorbates in the surroundings. This charge scattering and fluctuation arising from environmental effects can be effectively protected against via hBN passivation. Furthermore, unwanted impurities, gases, and adsorbates are inevitably incorporated at layer interfaces during the vdW stacking processes. As a crucial source of the charge fluctuation, the interface imperfection during the device fabrication process is also carefully considered. Therefore, the passivation and interface effects in device performances will be discussed in the following sections.

3.2. Passivation

3.2.1. Comparison of hBN to HfO2 deposition. The passivation effect of hBN in devices and optical properties compared to HfO2 encapsulation are shown in Fig. 9.46 The MoS2 transistor is encapsulated via the top hBN layer (Fig. 9a) and its electrical...
characteristics are compared to HfO₂ encapsulation synthesized via atomic layer deposition (ALD). As the temperature increases, the threshold voltage and mobility are measured in MoS₂ FETs with hBN encapsulation and HfO₂ encapsulation (Fig. 9b). The threshold voltage and normalized mobility as a function of temperature for HfO₂ drastically shifts due to the prominent environmental effects from the adsorbates, whereas the changes for hBN encapsulation are negligible. The time evolution of the environmental effects under ambient conditions was also characterized using comparative Raman and PL spectroscopy for HfO₂ and hBN encapsulation (Fig. 9c and d). After a few months, the Raman and PL peak intensities are severely degraded and the positions are shifted for HfO₂ encapsulation. Although the degradation mechanism of device performance and optical properties are still ambiguous, the possibility of a chemical reaction between MoS₂ and the Hf precursors during the ALD process at high temperature cannot be excluded because of the abrupt change in the Raman and PL spectra just after HfO₂ deposition, as shown in the green coloured spectra in Fig. 9c and d. On the other hand, the Raman and PL spectra for hBN encapsulation are not appreciable in addition to the negligible device performance changes.

3.2.2. For unstable 2D materials. The passivation of hBN is more effective for unstable 2D materials such as black phosphorus (BP) and HfS₂. The hBN encapsulation of BP in a glove box allows for simple and robust passivation. A schematic (left) and optical micrograph (right) of BP transistors partially passivated by a hBN layer are show in Fig. 10a. In the n-type region, the sheet conductance is > 5 mS per square and is not measurable for the bare BP part due to the oxidation of BP in ambient air, where electron traps are induced by oxygen point defects (Fig. 10b). Although such a degradation effect of BP is not prominent for the p-type transition region in the transistor behaviour, the morphology change caused by the oxidation degradation can be clearly observed in the AFM study. A noticeable surface change is not observed in the BN-encapsulated region (white dashed line), whereas the roughness is significantly developed in the unpassivated BP region after 5 days of exposure time in ambient air (Fig. 10c). As the exposure time to ambient air increases, the roughness continuously develops, in contrast to the negligible roughness changes for hBN-encapsulated BP.

Although HfS₂ is also a good candidate for electronic applications, few studies have been conducted because of...
its instability in air; Hf atoms easily react with oxygen in air, resulting in HfO$_x$ formation. The hBN passivation effects of HfS$_2$ have also been studied in a vacuum cluster system (Fig. 10e–g). All of the exfoliation, metallization, and passivation processes were conducted in connected vacuum glove boxes (Fig. 10e). Drain current transfer curves as a function of gate bias for HfS$_2$ FETs with and without hBN encapsulation were characterized in air. For the bare HfS$_2$ FET, a drain current level with a large hysteresis was drastically degraded after 2 days (Fig. 10f). However, for the hBN-encapsulated HfS$_2$ FET, the drain current level increased by three orders of magnitude and the hysteresis was prominently reduced (Fig. 10g). Moreover, such device properties are still similar even after one week of exposure to air, except for a slightly reduced current level. These experimental results imply the robustness of vdW interfaces between hBN and 2D materials. For 2D vdW heterostructures, the conventional ALD process results in poor interfaces due to chemical interactions, as discussed in Section 3.2.1, while the vdW interfaces of hBN allows robust environmental resistance even for unstable materials.

3.2.3. Interface and device performances. The interface properties are a key factor in determining the physical properties of thin 2D materials, as discussed in previous sections. However, defects such as adsorbates, bubbles, and gases are inevitably incorporated at the interfaces during artificial stacking processes for vdW heterostructures. The imperfection effect at hBN/TMD interfaces has been systematically investigated for carrier transport performances using MoS$_2$ FETs sandwiched between hBN layers. A schematic diagram of a hBN-sandwiched MoS$_2$ FET

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**Fig. 9** Passivation effects of hBN compared to HfO$_2$. (a) Schematic of a hBN-encapsulated MoS$_2$ FET with graphene contacts. (b) Comparative threshold voltage ($V_{th}$) and normalized mobility ($\mu/\mu_0$) as a function of the temperature for HfO$_2$- and hBN-encapsulated MoS$_2$ FETs, where $\mu$ and $\mu_0$ are the temperature dependent and room temperature mobilities, respectively. (c) Raman and (d) PL spectra of HfO$_2$- and hBN-encapsulated MoS$_2$ at various storage durations under ambient conditions. Reprinted with permission from ref. 46. Copyright 2015 American Chemical Society.

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**Fig. 10** Passivation effects of hBN for an unstable layered 2D channel. (a) Schematic of black phosphorus (BP) FETs with and without hBN-encapsulation and an optical micrograph of the FET. The scale bar is 3 µm. (b) Four-terminal conductance as a function of the backgate bias ($V_g$) with and without hBN-encapsulation of the BP FETs. (c) AFM topography of a 10 nm thick BP layer partially encapsulated by hBN flakes after 5 days in an Ar inert gas environment; scale bar: 4 µm. (d) Average roughness ($R_a$) of the AFM as a function of time in ambient air for the BP surface with and without hBN-encapsulation. Reprinted with permission from ref. 47. Copyright 2015 Nature Publishing Group. (e) Schematic of the integrated vacuum cluster system (left). Schematic and optical micrograph of devices with and without hBN-encapsulation fabricated in the cluster system (right). (f) Gate bias-dependent drain-current transfer curves of the FET of stability tests of the HfS$_2$ FET with and without hBN-encapsulation in ambient air. Reprinted with permission from ref. 48. Copyright 2016 American Chemical Society.
with Gr backgate and optical micrograph of the FET is shown in Fig. 11a and b. From the hysteresis and subthreshold swing (SS) in the drain current transfer curves as a function of gate bias for three different conditions, the interfacial trap density and interfacial trap density distribution per energy were calculated. Both values are clearly distinct for before and after encapsulation. Moreover, this reduced charge trap effect is much improved after annealing (Fig. 11c). For MoS\textsubscript{2} FET without hBN capulation, a prominent hysteresis was observed due to interface traps and the surface adsorption of unwanted moisture, molecules, and gases (Fig. 11d), while hBN encapsulation prevented the adhesion of adsorbates on the MoS\textsubscript{2} surface, and those at the MoS\textsubscript{2}/hBN and hBN/Gr interfaces were trapped, as shown in the inset of Fig. 11e. Therefore, such effect arising from the adsorbates is not fully removed, although the hysteresis and SS are significantly reduced after hBN encapsulation. Such trapped adsorbates at interfaces can be removed by thermal annealing. Thus, the hysteresis arising from the interface traps was almost negligible and the SS was much improved (Fig. 11f). The evolution of SS and mobility curves for the three different conditions of the FET are shown in Fig. 11g and h, respectively. For the annealed state, the SS curve reaches a thermal limit of 60 mV dec\textsuperscript{-1} and the mobility values reach 40 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}. Notably, hBN-encapsulation and annealing allow for the maximum on/off ratio and a nearly ideal limit of SS in the MoS\textsubscript{2} transistor in comparison to other published data (Fig. 11i).

3.3. Gate dielectrics

3.3.1. Layered gate dielectrics. The development of gate dielectric materials with good thin-film uniformity, good process compatibility, high crystallinity, and high dielectric constants has led to the performance improvement of next generation FETs for low power consumption, fast transport and switching speed, low leakage current, high on/off ratio, etc. Layered hBNs have been utilized as a promising gate dielectric material because of its atomic thickness tunability, ultraflat and defect-free surface, and easiness of forming heterostructures for numerous 2D vdW electronics, although the dielectric
constant of hBN ($\varepsilon \approx 4$) is lower than those of conventional high-$k$ gate dielectric materials such as Al$_2$O$_3$ ($\varepsilon \approx 9$), HfO$_2$ ($\varepsilon \approx 18$) or ZrO$_2$ ($\varepsilon \approx 25$). A lateral WSe$_2$ p–n diode with a hBN dielectric layer and two lateral backgate electrodes has been demonstrated (Fig. 12a–d). The bottom hBN gate dielectrics are transferred onto two gate electrodes and sequentially the WSe$_2$ FET is fabricated (Fig. 12a). The transient drain current curve shows ambipolar behaviour for positive to negative gate bias sweeping. Meanwhile, the red curve shows a near symmetric drain current curve as a function of drain bias for the fixed gate bias ($V_{g1} = V_{g2} = 8$ V) due to equal electron–hole doping, and the blue curve relates to the rectification of the p–n junction upon applying an opposite polarity of gate bias ($> +6.5$ V for electron doping and $> -6.5$ V for hole doping) to the two gates (Fig. 12b). Such a lateral p–n diode has also been realized using top hBN gate dielectrics. The integrated p–n junction on a photonic crystal silicon waveguide for optical communications is illustrated in Fig. 12c. On the basis of a similar mechanism as those shown in Fig. 12a and b, the electro-luminescence (EL) and exciton-to-waveguide coupling were demonstrated with the opposite bias polarity of the two top gates in the silicon waveguide coupled bilayer MoTe$_2$-device (Fig. 12d).

For high-performance 2D vdW FETs, the thickness of the gate dielectrics should be optimized. While a thicker layer is better for preventing breakdown and leakage, a thinner layer is favorable for maximizing the electrostatic effects. The hBN thickness effect in tunnelling has been intensively studied using a metal–insulator–metal diode and AFM measurements. Meanwhile, the dependence of the FET performance on the thickness of the hBN gate dielectric layers has been systematically investigated. The leakage current as a function of the gate bias and the model fittings for 4, 6, and 8 nm thick hBN backgate dielectric layers are shown in Fig. 12e. These were implemented using the device configuration of the MoS$_2$ FET, as discussed in Fig. 11. As the drain current increases, the leakage current behaves linearly for 4 nm-thick-hBN, implying direct tunnelling (DT). However, for 6 and 8 nm thick hBN, the near zero leakage current is dramatically increased at a higher gate bias due to Fowler–Nordheim tunneling (FNT). From the break-down electric field measurement as a function of the hBN thickness (Fig. 12f), the transition of the tunneling mode from DT to FNT can be clearly observed near a hBN thickness of 5 nm. The hBN thickness dependence of the on-current, off-current (left axis) and on/off ratio (right axis) at a drain voltage of 0.5 V and a gate bias ranging from $-5$ to $5$ V are shown in Fig. 12g. As the hBN thickness increases, the off-current generated by the tunneling leakage current is drastically decreased and saturated at a hBN thickness of $\approx 8$ nm, while the on-current is slightly reduced. Consequently, an optimum gate hBN thickness for the maximum on/off ratio ($\sim 10^6$) was determined to $\sim 8$ nm. Although the threshold voltage continuously decreases as the hBN thickness increases, the optimum thickness remains at less than 1 V, which is advantageous for low power consumption (Fig. 12h).

3.3.2. Flexible electronics. One of the unique features of 2D vdW electronics is their good adaptability for use in flexible electronics. The main bottleneck for high-performance flexible electronics is their good adaptability for use in flexible electronics. The main bottleneck for high-performance flexible electronics is their good adaptability for use in flexible electronics. The main bottleneck for high-performance flexible electronics is their good adaptability for use in flexible electronics. The main bottleneck for high-performance flexible electronics is their good adaptability for use in flexible electronics. The main bottleneck for high-performance flexible electronics is their good adaptability for use in flexible electronics. The main bottleneck for high-performance flexible electronics is their good adaptability for use in flexible electronics. The main bottleneck for high-performance flexible electronics is their good adaptability for use in flexible electronics. The main bottleneck for high-performance flexible electronics is their good adaptability for use in flexible electronics. The main bottleneck for high-performance flexible electronics is their good adaptability for use in flexible electronics. The main bottleneck for high-performance flexible electronics is their good adaptability for use in flexible electronics.

![Fig. 12 Layered gate dielectrics. (a) Schematic (top) and optical micrograph (bottom) images of a WSe$_2$ lateral p–n diode with multi-layer hBN backgate dielectrics and two lateral backgate electrodes ($V_{g1}$ and $V_{g2}$). (b) The drain current transfer curve as a function of the gate bias ($V_{g1}$, $V_{g2}$) of the p–n diode with ambipolar behaviour. Inset: The drain current transfer curve as a function of the drain bias ($V_{g1}$) curves for $V_{g1} = V_{g2} = 8$ V (the red curve is for the equal electron–hole doping) and $V_{g1} = -8$ and $V_{g2} = 8$ V (the blue curve is for rectification). Reprinted with permission from ref. 50. Copyright 2014 Nature Publishing Group. (c) Schematic and (d) EL and PL spectra (at 6 K and 300 K) of a MoTe$_2$ lateral p–n diode with multi-layer hBN top gate dielectrics and two lateral top gate electrodes ($V_{g1}$ and $V_{g2}$). Reprinted with permission from ref. 51. Copyright 2017 Nature Publishing Group. (e) Gate-hBN thickness dependence of the leakage current ($I_{\text{leak}}$) as a function of the gate bias ($V_g$) of the MoS$_2$ FET in Fig. 10(a) and the data fitting using the direct tunneling (DT) and Fowler–Nordheim tunnelling (FNT) analytical models. (f) Break-down electric field ($E_{\text{break}}$) at $I_{\text{leak}} = 1$ nA, and (h) off-current, on-current and on/off ratio curves as well as (g) the threshold voltage ($V_{\text{th}}$) as a function of the gate hBN thickness ($t_{\text{h-BN}}$) of MoS$_2$ FETs. Reprinted with permission from ref. 49. Copyright 2018 Institute of Physics Publishing.](image-url)
electronics is mechanical robustness for situations where bending or stretching is required. In contrast to metallic films that are ductile, conventional dielectric films are brittle. Meanwhile, layered hBNs have been widely studied as dielectric gate and passivation layers not only for robust substrates but also soft substrates, due to the high mechanical strength of hBN.30,52,53 A MoS₂ FET on a hBN gate dielectric layer with a graphene gate has been prepared on polyethylene naphthalate (PEN) substrates (Fig. 13a–c) and the optical micrograph is shown in Fig. 13a.30(192,640),(307,662) Even up to 1.5% bending strain, the changes in the transfer characteristics (Fig. 13b) and relative field-effect mobility variation (Fig. 13c) as a function of applied strain are negligible, which implies the robustness of hBN with a thickness ranging from 10 to 30 nm when used as a gate dielectric layer in flexible electronics. Vertical tunneling FETs consisting of a WS₂ tunneling spacer sandwiched by graphene electrodes on hBN gate dielectric layers also demonstrate a robust device performance for flexible substrates. The optical micrographs in reflection and transmission mode as well as the device bending image of the WS₂ tunnelling FET stacked on flexible polyethylene terephthalate (PET) films are shown in Fig. 13d–f.52,53 Under an applied bending curvature of 0.05 mm⁻¹, the switching characteristics based on vertical tunneling for PEF substrates are similar to those for Si substrates, implying insensitivity to bending (Fig. 13g).53

3.4. Tunneling layer

3.4.1. Quantum tunnel junction. Quantum transport phenomena allow for high speed and low power switching, such as tunneling FET and spintronics.55,56,174–180 In terms of the tunneling-transport, although a controlled thickness and defect-free tunneling barrier is the key for a reliable device, such issues are still challenging in conventional thin film deposition processes. Meanwhile, the layer tunability and ultra-flat nature of hBN allow for the study of quantum tunneling at the atomic scale.54,55,181,182 A resonant tunneling effect has been demonstrated with the hBN tunnel barrier (≤6-layer hBN corresponding to ~2 nm) sandwiched by bilayer graphene, where the Fermi levels are modulated via the backgate bias (Fig. 14a).54,55 In this device structure, quantum tunneling phenomena between graphenes are modulated by the resonance effect during carrier transport, where the thin hBN layer acts as a tunneling barrier for the 2D carrier system. The resonantly enhanced tunneling current and negative differential resistance are clearly observed (Fig. 14b). Upon increasing the applied bias between the graphene electrodes, the interlayer tunneling current reveals a resonant peak shape. Moreover, the peak intensity is enhanced and the peak position shifts to a higher bias level as the backgate bias increases. Such a resonant tunneling mechanism is depicted in Fig. 14c. In the double well system isolated by a potential barrier, a resonant standing-wave within the well between the barriers can be allowed, when the energy eigenstate of the injected carriers is aligned to the energy eigenstate of the carriers in the opposite well. While the resonant tunneling probability of the electrons through the barrier increases for the aligned energy state (see the peak in Fig. 14c), the probability is reduced for the
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misaligned energy state due to an out-of-resonance condition (see the valley in Fig. 14c). Therefore, the resonant tunneling current is tunable by modulating $V_{\text{TL}}$ and $V_{\text{BG}}$ for the energy matching and negative differential resistance occurs, as shown in Fig. 14b.

A magnetic tunnel junction consisting of two ferromagnetic contacts separated by a thin oxide tunnel barrier is a promising platform for spintronics. Manipulating the tunneling magnetoresistance with an optimal junction resistance is a key for magnetic random access memory and spin-transfer torque devices, where the tunnel barrier for tunneling magnetoresistance should be precisely controlled. However, uniform thickness control at the atomic level and a defect-free structure are still a challenge to achieve in metal oxides synthesized using conventional thin film deposition methods. Meanwhile, hBN has been used as a solution for a spin barrier issue in magnetic tunnel junctions (Fig. 14d). Monolayer hBN grown by CVD allows for quantum tunneling of spin-polarized electrons. When the magnetization of ferromagnetic electrodes is in a parallel orientation, the tunneling probability of the spin-polarized electrons through the hBN barrier is higher than that in the anti-parallel orientation, which results in a resistance change across the FM junction. Such a concept has been experimentally demonstrated. The dashed area in the optical micrograph (Fig. 15b) shows the light emission contrast with the red colour in the EL image (Fig. 15c). Comparative PL and EL spectra were measured for the device at 7 K (Fig. 15d). Each spectrum is in good agreement with the typical excitonic emission for MoS2.

3.4.2. Tunnel junction optoelectronics. hBN tunnel junctions are also widely used in light-emitting diodes and photodetector. Band-structure engineering in quantum-well-like vdW heterostructures results in a novel type of light-emitting diodes. The cross sectional schematic diagram (top) of the single quantum well (SQW) heterostructure of hBN/Gr$_2$/2hBN/WS$_2$/2hBN/Gr$_2$/hBN and its band diagram for applied bias (bottom) are shown in Fig. 15a. Under an applied bias between the top (Gr$_2$) and bottom (Gr$_2$) graphenes, the Fermi level of Gr$_2$ rises above the MoS$_2$ conduction band. Meanwhile, the Fermi level of Gr$_2$ falls below the MoS$_2$ valance band, which allows for charge tunnelling from Gr to MoS$_2$ through hBN tunnel barriers. As a result, the accumulated electrons and holes form excitons in the MoS$_2$ layer. Such a concept has been experimentally demonstrated. The dashed area in the optical micrograph (Fig. 15b) shows the light emission contrast with the red colour in the EL image (Fig. 15c). Comparative PL and EL spectra were measured for the device at 7 K (Fig. 15d). Each spectrum is in good agreement with the typical excitonic emission for MoS$_2$.

Another type of light emitting diode based on a hBN tunnel barrier is a plasmonic antenna-coupled photodetection device. When a bias is applied to metal–insulator–metal junctions, the electrons tunnel through the insulator from occupied to unoccupied states between the electrodes. In this process, the energetic hot electrons are relaxed via a thermalization process and the inelastically tunnelled electrons excite surface plasmons. This process results in far-field emission decay (see the inset of Fig. 15e). Such light generation via inelastic electron tunnelling has been investigated using a plasmonic nano-antenna patterned metal–insulator–metal diode possessing the hBN tunnel barrier (Fig. 15e), where the slot antenna resonantly enhances light emission. The bias-induced light emission images from four devices with different slot sizes of 150 $\times$ 50, 250 $\times$ 50 and

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**Fig. 14** Quantum tunnel junctions. (a) Schematic of the band structures for a resonant tunneling hBN layer sandwiched by top and bottom graphene. (b) Interlayer tunnelling current $I_{\text{int}}$ as a function of the interlayer tunnelling bias $V_{\text{TL}}$ for various backgate biases $V_{\text{BG}}$. Reprinted with permission from ref. 54. Copyright 2015 American Chemical Society. (c) Schematic of the resonant tunnelling concept. Eigen-energy matching (resonance) and mismatching (out of resonance) of the injected carrier with the carrier in the potential well. Reprinted with permission from ref. 55. Copyright 2017 Institute of Physics Publishing. (d) Schematic of the spin-polarized tunnelling of a hBN magnetic tunnel junction. (e) Py/hBN/Co magnetic tunnel junction with a cross bar geometry. (f) Tunnelling magnetoresistance (TMR) plot under in-plane magnetic ($B$) field sweeps. Arrows: up-down $B$ field sweep directions. Reprinted with permission from ref. 56. Copyright 2015 Springer Nature.
The light emission spectra (left axis) and light transmission enhancement (right axis) are displayed in Fig. 15g. While a broad spectral feature is observed in device 0, all devices with nanostructures exhibit strongly enhanced light emission intensity at a short wavelength regime due to tunnelling electron interactions with the surface plasmon resonance.

The hBN tunnel barrier is also applicable to photodetectors for ultrahigh detectivity. In general, photodetectivity is determined by the competition between the photoresponsivity and on/off current ratio. Although photoconductor-type devices show high responsivity, the large drain bias increases the dark current, sacrificing the on/off current ratio. Conversely, while photovoltaic-type devices display low responsivity but a high on/off ratio. However, in tunnelling-based photodetectors with a graphene/hBN/MoS2 structure, an optimum hBN thickness of ~7 nm has been shown to result in both high photoresponsivity and on/off current ratio, which is strong contrast to other photodetector and photovoltaic type devices.

3.4.3. Tunnel junction memory. hBN tunnel junctions exhibit promising potential as floating gate dielectrics for memory devices. In contrast to three terminal floating gate memories consisting of a source, a floating gate, and a drain, tunnelling based vdW memory involves a simple device architecture and a high potential for use in flexible electronics. A device architecture with two terminals using vertically stacked MoS2/hBN/Gr heterostructures and operation mechanisms is illustrated in Fig. 16a and b. As the programming bias (drain bias < −6 V) is applied, large potential differences between the source and drain allow for electron tunnelling through the hBN barrier (< ~10 nm thick) and charge storage in the graphene. On the other hand, when the erasing bias (drain bias < −6 V) is applied, the injected holes through hBN erase the stored charges in the graphene (Fig. 16b). The drain current curve as a function

350 × 50 nm² for devices 1, 2 and 3, as well as an unstructured reference device 0, respectively, are presented in Fig. 15f. The corresponding light emission spectra (left axis) and light transmission enhancement (right axis) are displayed in Fig. 15g. While a broad spectral feature is observed in device 0, all devices with nanostructures exhibit strongly enhanced light emission intensity at a short wavelength regime due to tunnelling electron interactions with the surface plasmon resonance.

The hBN tunnel barrier is also applicable to photodetectors for ultrahigh detectivity. In general, photodetectivity is determined by the competition between the photoresponsivity and on/off current ratio. Although photoconductor-type devices show high responsivity, the large drain bias increases the dark current, sacrificing the on/off current ratio. Conversely, while photovoltaic-type devices display low responsivity but a high on/off ratio.

### Eq. 1

\[ I_{\text{ph}} / I_{\text{dark}} \]

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Fig. 15 Tunnel junctions for optoelectronics. (a) Cross sectional schematic (top) and band diagram under a bias application (bottom) of a single quantum well (SQW) heterostructure for an LED. (b and c) Optical micrograph and PL image; scale bar: 10 μm, and (d) PL and EL spectra for the SQW light-emitting device with MoS2 monolayers. Reprinted with permission from ref. 58. Copyright 2015 Nature Publishing Group. (e) Schematic, (f) light emission images, and (g) light emission spectra (open circles) in comparison with the optical transmission enhancement (solid line) of a plasmonic antenna-coupled photoemission device based on a hBN tunnel junction. Reprinted with permission from ref. 59. Copyright 2015 Nature Publishing Group. (h) Schematic of a photodetector consisting of MoS2/hBN/Gr and (i) its photodetectivity versus the \( I_{\text{ph}} / I_{\text{dark}} \) ratio as a function of hBN thickness compared to published data. \( I_{\text{ph}} \): photocurrent. \( I_{\text{dark}} \): dark current. Reprinted with permission from ref. 60. Copyright 2016 American Chemical Society.
of the drain bias of this two-terminal tunnelling random access memory (TRAM) is displayed in Fig. 16c with a memory window region. This reversible memory effect based on tunnelling is robust and lasts over a large number of cycles. The program-merge/erasing cyclability reaches an on/off ratio of over $10^6$ (Fig. 16d). The memory performance of TRAM is compared with other two terminal memories such as resistive random access memory and phase-change random access memory in Fig. 16e. The TRAM exhibits a lower off current (left panel) and a high on/off ratio (right panel) versus the reading voltage normalized by the memory window voltage compared to other memories. Such a low off current is advantageous because effective charge tunnelling through hBN and charge storage in graphene reduce the off-state power consumption and data sensing error from circuit noise. Moreover, the main advantage of this TRAM device architecture is its adaptability on flexible substrates. The bending image and optical micrograph of TRAM on flexible polyethylene terephthalate (PET) substrates are displayed in Fig. 16f and g. The on/off switching ratio of $B10^3$ retains up to 0.5% strain (Fig. 16h).

3.5. Coulombic interactions

One of the unique features of 2D layered semiconductors is a reduced dielectric screening effect. This feature allows for strong exciton binding and stable excitonic emission even at room temperature. Even in vdW bilayers or heterobilayer structures, such excitonic binding is strong so that interlayer or indirect excitons can be observed. The exciton binding in a bilayer system is modulated by the interlayer space. Here, atomically thin hBN is a good candidate for modulating Coulombic interactions.61–64 The conceptual indirect (or interlayer) excitons in a MoS$_2$/hBN bilayer with a two hBN space is represented in Fig. 17a.61 This concept for Coulombic interaction modulation has been demonstrated by MoS$_2$/WSe$_2$ heterobilayers.62 As the hBN spacer number increases, the interlayer peak position blue-shifts due to the reduced interlayer exciton binding energy (Fig. 17b and c). The manipulation of the Coulombic interaction as a function of the hBN layer number was theoretically investigated for MoS$_2$/WS$_2$ heterobilayers, as shown in Fig. 17d.63 The intra and interlayer exciton binding energies are displayed as a function of the number of intercalating vacuum (left panel) and hBN (right panel) layers. As the hBN number increases, the intralayer exciton binding energies increase due to a reduction in the dielectric screening effects, while the interlayer exciton binding energies are reduced due to the Coulombic field between the layers. The hBN spacer is also used for Coulombic drag devices.64,190 The measurement set-up and detailed device structure, where two bilayer graphenes are separated by a 3 nm-thick hBN layer are illustrated in Fig. 17e and f. In this device, under a magnetic field at low temperature, strong Coulombic coupling across the hBN layer allows for quantum Hall drag between the graphene layers, as shown in Fig. 17g.

3.6. Contact resistance

Although emerging electronic devices based on 2D semiconductors have been highlighted for post-CMOS electronics, the critical bottleneck for high-performance electronic devices is the metal/semiconductor contacts. In contrast to conventional bulk semiconductors, a lack of dangling bonds on TMdC surfaces limits metal/TMdC hybridization at the contact.191 Moreover, TMdCs such as MoS$_2$, with a large band gap, form Schottky barriers with various metals.192–194 Among the many methods investigated to solve this issue, a CVD-grown hBN buffer was investigated as one promising platform.65,66 A schematic diagram of a monolayer MoS$_2$ FET, where monolayer hBN is inserted between Co metal and monolayer MoS$_2$ for the work.
function modulation of Co and tunnel barriers, is illustrated in Fig. 18a. The drain current transfer curve as a function of the backgate bias shows that the current level is prominently increases upon a reduction in the temperature (Fig. 18b). The hBN effect is dramatically observed in comparative drain current curves as a function of the drain bias for various gate biases at 1.7 K (Fig. 18c and d). The drain current level is two orders of magnitude higher for the device with hBN than that without hBN. Moreover, the estimated Schottky barriers for the device with hBN are two times smaller (Fig. 18e) than those for the device without hBN (Fig. 18f).

The hBN role in contact resistance is also effective for multilayer TMdCs. The SEM image (top) and cross-sectional schematic (bottom) of a few-layer MoS₂ transistor with hBN tunnelling barrier with 1–2 layers for metal contact are shown in Fig. 18g. The atomic interface image for the hBN interlayer between MoS₂ and Ni is shown in the high resolution transmission electron microscopy image (Fig. 18h). For the overall gate bias, the measured contact resistance for the device without hBN is one order of magnitude higher (Fig. 18i) than that with hBN (Fig. 18j). Two possible scenarios are proposed: a blocked deep state and dipole formation. At the interface of the metal–semiconductor, the decayed electron wavefunction from the metal changes the interface state of the semiconductors. Such a metal induced gap state yields a high Schottky barrier, as shown in Fig. 18k. However, the hBN interlayer blocks the deep state formation at the interface so that the Schottky barrier can be reduced (Fig. 18l). Meanwhile, the dipole formation at the interface of the metal–insulator–semiconductor can neutralize the charge polarity, resulting in effective Schottky barrier reduction (Fig. 18m). In these processes, the thin monolayer hBN allows for direct tunnelling so that the resulting contact resistance is reduced.

4. Summary and perspective

hBN plays an important role as a building block in diverse 2D vdW electronics. To realize large-area electronics, the synthesis of hBN and its in-plane and vertical heterostructures on the wafer scale have been developed using CVD. Surface-mediated growth on catalytic Cu, Pt, and Au foils of monolayer hBN films has been developed. It starts with the growth of triangular hBN grains at random orientations on the substrate and then the grains merge to form a polycrystalline hBN film. However, the quality of the hBN film is not as high as that of SC-hBN.
Therefore, it is further required to develop (1) the growth of single-crystal monolayer hBN films free from wrinkle formation, (2) direct growth on dielectric substrates without involving transfer, and (3) ensure reproducibility of the hBN growth.

Precipitation (or segregation) after dissolving B and N atoms in the Fe substrate during the cooling process is used to synthesize the multilayer hBN film. The thickness of the hBN layer is controlled by either the thickness of the Fe film or the solubility of the B and N atoms in Fe. However, the thickness of the hBN film has not been precisely controlled yet. The remaining issues for the synthesis of multilayer hBN films are (1) the growth of wrinkle-free and single-crystal multilayer hBN films and (2) the control of the thickness and uniformity of the hBN film.

Vertical 2D/hBN vdW heterostructures are prepared by the direct synthesis of 2D materials on single-crystal hBN flakes. To grow graphene on insulating single-crystal hBN flakes, a gaseous catalyst (silane) and PECVD are employed to effectively decompose the hydrocarbon used as a carbon precursor. For other 2D/hBN vertical heterostructures, the direct growth of TMdCs (MoS₂, WS₂, and ZrS₂) on a hBN substrate is achieved in a similar manner to the growth of the materials on SiO₂/Si substrate. All of the 2D materials are grown by vdW epitaxy on single-crystal hBN substrates. However, the two different types of TMdC grains, on-top and inverse triangles, limit the growth of single-crystal 2D materials. In addition, it has been found that hBN wrinkles disturb vdW epitaxy. Therefore, (1) the preparation of a wafer-scale single-crystal hBN substrate free of wrinkles and (2) the control of the growth kinetics for van der Waals epitaxy, such as layer-by-layer growth, should be developed. Furthermore, the control of the lattice orientation of triangular-shaped TMdC grains toward one orientation is necessary to grow vertical single-crystal TMdC/hBN heterostructures.

Wafer-scale 2D/hBN vertical heterostructures are realized by a two-step growth route: the growth of a polycrystalline hBN film, followed by the growth of the 2D material. To avoid the etching of hBN during the growth of graphene on the hBN substrate, new precursors, nickelocene as a catalyst and a carbon precursor, are introduced. Meanwhile, co-segregation of graphene and hBN from the sandwich structure of the C-doped Ni film/B, N source/Ni film has also been investigated. For the growth of TMdCs on hBN film, the careful choice of the growth substrate is required due to the chemical reaction between the chalcogens and metal substrate used for the hBN growth. Until now, Au foils and Ni–Ga alloys have been used exclusively as growth substrates. 2D materials grown on polycrystalline hBN films exhibit a polycrystalline structure, indicating that vdW epitaxy could not occur. The challenging issues that remain for 2D/hBN vertical heterostructures on the wafer scale are (1) the synthesis of a single-crystal hBN substrate on the wafer-scale, (2) the development of 2D/hBN...
van der Waals epitaxial growth, and (3) the search for new substrates with high resistance toward chalcogens, as well as exclusive alloy formation.

In-plane 2D–hBN heterostructures have only been demonstrated using a CVD approach. The alternative supply of borazine and ethylene on Ru(0001) allows for the homogeneous epitaxy of a Gr–hBN in-plane heterostructure. For a Gr–hBN in-plane structure, either the selective growth of graphene at the etched region between the hBN regions or the conversion of hBN to graphene on the patterned Pt region are introduced. In-plane hBN–MoS2 has been grown using a seeding promoter (PTAS), which is likely deposited on the SiO2/Si substrate rather than the hBN surface. A similar approach has been followed to prepare graphene–MoS2 and WS2–MoS2 in-plane heterostructures. The remaining issues for hBN–2D in-plane heterostructures are (1) the development of in situ patterned homoepitaxial growth for the creation of a sharp heterojunction at the wafer scale and (2) the investigation of other in-plane 2D–hBN heterostructures.

To construct well-defined vertical 2D vdW heterostructures, artificial transfer has been developed. This allows for the choice of the stacking sequence with diverse 2D materials, as well as the production of high quality vertical 2D/hBN heterostructures. Monolayer 2D materials have been prepared by mechanical exfoliation. The surface cleaning of a SiO2/Si substrate by oxygen plasma and heat treatment helps to achieve mining whether “pick-up” (during the stacking process plays an important role in determining whether “pick-up” (Tsub ~ 40 °C) or “drop-down” (Tsub > 110 °C) occurs. Furthermore, the slight tilt of the substrate by a few degrees during drop-down significantly prevents blister formation between 2D materials. New techniques for completely preventing blister formation between 2D materials still require further development.

As a dielectric material in 2D vdW electronics, we have reviewed the various functionalities of hBN layers. For high performance in electronic devices, including low-power consumption, fast-operation, high on/off ratio, and high photodetectivity, there are numerous advantages to using hBN, such as high crystallinity, thickness controllability at the atomic layer scale, dangling-bond-free surfaces from the viewpoint of charge fluctuation, passivation, and gate dielectrics, especially for 2D vdW FETs. Among the features of hBN described above, the ability to control the uniformity and thinness of a few atomic layers is important for their use in quantum tunneling devices, including resonant tunneling transistors, magnetic tunnel junctions, tunneling memory, tunneling phototransistors, and tunneling light emitting devices. Moreover, the thinness of the layers can be utilized for studying the Coulombic interactions between 2D layers and Schottky barriers in contact resistance.

Nevertheless, numerous challenges still remain for practical applications and the wafer-scale manufacture of hBN. As discussed in the sections on charge fluctuation and passivation, interface imperfections between hBN and active layers affect the carrier transport and device reliability. While direct growth of each layer on substrates is a promising way for solving such an issue, the direct growth of hBN with high crystallinity and uniformity is still challenging because of the high temperature required for the synthesis of hBN. Although transferring hBN layers synthesized using a CVD method on catalytic metal substrates is an alternative way, the remaining issues, including wrinkling due to the large thermal mismatch between the substrates, inhomogeneous layer thickness, and defective structures at the grain boundaries of metal substrates, are a bottleneck for the CVD growth. hBN also contains many different type of vacancies from a microscopic point of view, which can be utilized for single photon sources due to deep trap emission in the band gap. Such vacancy induced traps are intentionally used for optoelectronics, where electron beam irradiation increases the vacancy density. However, the evolution of defects by charge fluctuation sources via external energies should be carefully considered with respect to the manufacturing processes of electronic devices. Therefore, defect generation and healing mechanisms should be investigated from the microscopic point of view for future hBN applications.

Conflicts of interest

There are no conflicts to declare.

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