Methods

Synthesis of Bernal-Stacked h-BN

Bernal-stacked few-layer h-BN is synthesized on copper and iron foils using LP-CVD. Similar to reference^{1,2}, ammonia-borane powder was used as a stoichiometric B and N precursor, and a two-heating-zone system (Fig. S1) is used to separately control the temperatures of the solid precursor and transition metal catalyst.

Prior to the LP-CVD process, the metal foil catalyst undergoes minimal pretreatment. Copper foils are soaked in glacial acetic acid 10 minutes followed by rinsing with DI water. Iron foils are soaked 10 minutes in acetone followed by rinsing with IPA and DI water. The foil is then annealed for 1-2 hours at low pressure with a flow of 100 sccm H₂ and 300 sccm Ar at 1025 °C for copper or 1100 °C for iron.

After annealing, the argon gas flow is turned off, the hydrogen gas flow is set between 100-200 sccm, and 100 mg of ammonia-borane powder, loaded in a one-end sealed quartz tube upstream of the metal catalyst, is heated to 80 °C. The byproducts of the thermal decomposition of the ammonia-borane diffuse 6 inches before they are pushed downstream by the hydrogen carrier gas toward the transition metal foil. After 20-60 minutes of h-BN growth, the hydrogen flow is reduced to 10 sccm, the precursor is quickly cooled, and the metal foil is allowed to cool at a rate of >10 C/min. For the studies in this paper, we focus on material grown on the bottom of the foil which varies from that on the top.

TEM Characterization of h-BN

We performed high-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) on the h-BN to confirm its stacking and orientation.^{3–6} The as-grown CVD h-BN was transferred to quantifoil holey carbon TEM grids by a direct transfer process.⁷

First, the grids are adhered to the h-BN on copper foil using a droplet of isopropanol. The copper foil is then dissolved by floating in sodium persulfate (10% w/v), and the grid is subsequently floated in deionized water in order to rinse off any adsorbed salts.

HR-TEM was carried out at 80 kV using the TEAM 0.5 microscope with spherical aberration correction ($C_s = -15$) and a monochromator. Exit wave reconstruction is used to create atomic resolution images from 80-100 raw images in a focal series. SAED patterns were acquired using a JEOL 2010 transmission electron microscope (TEM) at 80 KV.

Computational methods

In order to gain a full understanding of the effects of stacking in hexagonal BN, we conduct a complementary first-principles study using density functional theory (DFT) with the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE GGA)³⁷ and norm-conserving pseudopotentials.⁸ We employ the QUANTUM ESPRESSO software package⁹ with a 160 Ry plane-wave energy cutoff for the pseudo Kohn-Sham wavefunctions. For bulk (bilayer) simulations, we use a $12 \times 12 \times 8$ ($12 \times 12 \times 1$) Monkhorst-Pack k-point mesh. All atomic coordinates are relaxed until the forces on all the atoms are less than 10^{-3} Ry/ a_0 in all axial directions, where a_0 is the Bohr radius. To simulate free-standing BN bilayers, we insert a ~14 Å thick vacuum between the periodic copies of the slab.¹⁰ We have found the in-plane lattice constants of all the high-symmetry BN stackings to be equal (2.51 Å) within the precision of the calculation; hence we have used the same value for the lattice constants of all bilayers. In order to include the interlayer van der Waals (vdW) interactions, we have used the Tkatchenko-Scheffler (TS) correction, where a *C*₆/*R*⁶ correction to the ionic potential is applied with *C*₆ coefficients derived from first-principles,¹¹

The rationale behind our usage of GGA with the TS vdW correction is its successful prediction of interlayer distances. For the commonly grown AA' stacked BN, the experimental interlayer distance is 3.33 Å.¹² We have found that Perdew-Zunger local density approximation (PZ LDA)¹³ results in an interlayer distance of 3.23 Å without a van der Waals correction, and 2.91 Å with a Grimme-type dispersion correction.¹⁴ This is consistent with the literature where it has been noted that LDA underestimates interlayer distances in van der Waals materials.^{15,16} On the other hand, our PBE GGA results are 4.24 Å without a van der Waals correction, 3.08 Å with Grimme vdW, and 3.33 Å with TS vdW (a perfect match with the experimental value). The fact that GGA without a correction overestimates interlayer distances is also consistent with the literature.^{17–20} Finally, we have verified the observation made by Ref. ¹⁸ that the van der Waals correction sets the interlayer distance but does not significantly change the relative total energies of the different layer stackings. However, as we shall discuss below, because the energy differences are very small (a few meV per cell), it is important to include the van der Waals term for a correct picture of the energy landscape.

Furnace Stuff

Figure S1: Photograph of LP-CVD Setup



T_0 - Solid Precursor T_1 - Hot Zone(1050° C) BH₃NH₃(70-90° C) with Metal Catalyst



Figure S2: Selected Area Electron Diffraction (SAED) – Experimental and Simulation

(Upper Left) Relative intensities of the first order diffraction peak (shown left) to the second order diffraction peak (right) in the diffraction pattern in Fig. 3c. (Upper Right) The diffraction pattern from Fig. 3c. (Bottom Left) A simulated diffraction pattern for bulk AA' stacked h-BN using the Single Crystal software package. (Bottom Center) A simulated diffraction pattern for bulk AB stacked h-BN. (Bottom Right) A simulated diffraction pattern for bulk ABC stacked h-BN.





An Aberration corrected HR-TEM focal series reconstruction of a mixed monolayer, bilayer, and trilayer region of AB stacked h-BN from which the images shown in Fig. 3 d-e are cropped.

Figure S4: SEM images of h-BN synthesized with Low $\rm H_2$ versus time

h-BN CVD on copper with low (20 sccm) $\rm H_2$ flow



15 min

30 min

60 min

References

- ¹ K.K. Kim, A. Hsu, X. Jia, S.M. Kim, Y. Shi, M. Hofmann, D. Nezich, J.F. Rodriguez-Nieva, M. Dresselhaus, T. Palacios, and J. Kong, Nano Lett. **12**, 161 (2012).
- ² S.M. Gilbert, G. Dunn, A. Azizi, T. Pham, B. Shevitski, E. Dimitrov, S. Liu, S. Aloni, and A. Zettl, Sci. Rep. 7, 15096 (2017).
- ³ B. Shevitski, M. Mecklenburg, W.A. Hubbard, E.R. White, B. Dawson, M.S. Lodge, M.
- Ishigami, and B.C. Regan, Phys. Rev. B 87, 45417 (2013).
- ⁴ J. Ping and M.S. Fuhrer, Nano Lett **12**, 26 (2012).
- ⁵ J.H. Warner, M.H. Rümmeli, A. Bachmatiuk, and B. Büchner, ACS Nano 4, 1299 (2010).
- ⁶ S. Lee, K. Lee, and Z. Zhong, Nano Lett. **10**, 4702 (2010).
- ⁷ W. Regan, N. Alem, B. Alemán, B. Geng, Ç. Girit, L. Maserati, F. Wang, M. Crommie, and A. Zettl, Appl. Phys. Lett. **96**, 113102 (2010).
- ⁸ D.R. Hamann, Phys. Rev. B **88**, 85117 (2013).
- ⁹ P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L.
- Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R.
- Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F.
- Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G.
- Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, and R.M. Wentzcovitch, J. Phys. Condens. Matter **21**, 395502 (2009).
- ¹⁰ M.L. Cohen, M. Schlüter, J.R. Chelikowsky, and S.G. Louie, Phys. Rev. B 12, 5575 (1975).
- ¹¹ A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. **102**, 73005 (2009).
- ¹² J. Wang, F. Ma, and M. Sun, RSC Adv. 7, 16801 (2017).
- ¹³ J.P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
- ¹⁴ S. Grimme, J. Comput. Chem. **27**, 1787 (2006).
- ¹⁵ G. Kern, G. Kresse, and J. Hafner, Phys. Rev. B **59**, 8551 (1999).
- ¹⁶ A. Marini, P. García-González, and A. Rubio, Phys. Rev. Lett. 96, 136404 (2006).
- ¹⁷ H. Rydberg, M. Dion, N. Jacobson, E. Schröder, P. Hyldgaard, S.I. Simak, D.C. Langreth, and
- B.I. Lundqvist, Phys. Rev. Lett. 91, 126402 (2003).
- ¹⁸ N. Marom, J. Bernstein, J. Garel, A. Tkatchenko, E. Joselevich, L. Kronik, and O. Hod, Phys. Rev. Lett. **105**, 46801 (2010).
- ¹⁹ R.M. Ribeiro and N.M.R. Peres, Phys. Rev. B **83**, 235312 (2011).
- ²⁰ G. Constantinescu, A. Kuc, and T. Heine, Phys. Rev. Lett. **111**, 36104 (2013).