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Article

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Chemical Vapor Deposited Hexagonal Boron Nitride as a Scalable Template for High-Performance Organic Field-Effect Transistors

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ABSTRACT: Organic field-effect transistors have gained much attention for their potential use in low-cost, large-area, flexible electronics. High-performance organic transistors require a low density of grain boundaries in their organic films and a reduction of charge traps at the semiconductor-dielectric interface for efficient charge transport. In this respect, the role of the dielectric material is crucial because it primarily determines the growth of the film and the interfacial trap density. Here, we demonstrate the use of chemical-vapor-deposited hexagonal boron nitride (CVD h-BN) as a scalable growth template/dielectric for high-performance organic field-effect transistors. The field-effect transistors based on C₆₀ films grown on single-layer CVD h-BN exhibit an average mobility of 1.7 cm²V⁻¹s⁻¹ and a maximum mobility of 2.9 cm²V⁻¹s⁻¹ with on/off ratios of 10⁷. The structural and morphology analysis shows that the epitaxial, two-dimensional growth of C₆₀ on CVD h-BN is mainly responsible for the superior charge transport behavior. We believe that CVD h-BN can serve as a growth template for various organic semiconductors, enabling large-area, high-performance flexible electronics.

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3 Organic field-effect transistors (OFETs) have been investigated for their high potential in low-
4 cost, large-area flexible electronics. Efficient charge carrier transport in OFETs is critical for
5 extending the scope of their applications.^{1, 2} The grain boundaries in polycrystalline organic
6 semiconductor films and trap sites at the organic semiconductor/dielectric interface have
7 detrimental effects on charge transport.³⁻⁵ Therefore, it is of great importance to reduce the
8 density of grain boundaries by engineering the organic film growth/deposition process and to
9 lower interfacial trap density by optimizing dielectric materials for OFETs.

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21 There have been significant efforts to increase the grain size in organic films.⁶⁻⁸ For solution-
22 processible organic materials, a variety of processes have been introduced to achieve highly
23 ordered organic films. Notably, using the solution shearing method, we have previously achieved
24 the growth of millimeter-wide and centimeter-long single-crystalline domains of TIPS-pentacene
25 that exhibits high charge carrier mobility.⁷ For vapor deposited organic materials, increasing
26 substrate temperature during deposition is one of the simpler ways for increasing grain sizes.^{6, 8}
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28 However, fabrication processes at high temperatures above 150°C limit the use of some plastic
29 materials required for flexible applications. Since flexible electronics are one of the important
30 target applications for organic semiconductors, a method that can enlarge grain sizes at low
31 temperatures – below 150°C – is highly desirable.

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46 Atomically thin 2D materials such as graphene and hexagonal boron nitride (h-BN) have been
47 recently investigated as growth templates for organic films.⁹⁻¹⁴ These 2D materials are atomically
48 flat without dangling bonds, which can minimize the charge traps at the organic-2D material
49 interface. Moreover, their van der Waals interactions with organic molecules can enable the
50 epitaxial growth of organic films, increasing grain sizes.¹¹⁻¹³ Indeed, the epitaxial growth of C₆₀,
51 an n-type organic semiconductor, on graphene has been observed.¹³ The low trap density at
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graphene/C₆₀ interface has been also demonstrated by effective modulation of the Schottky barrier between graphene and C₆₀.^{13, 15} Furthermore, researchers have shown that h-BN can serve as an ideal dielectric layer for graphene devices, with its atomically flat surface, low trap density, and reduction of electron-phonon scattering.¹⁶⁻¹⁹ The epitaxial growth of other organic molecules such as rubrene and dioctylbenzothienobenzothiophene (C₈-BTBT) on mechanically exfoliated h-BN flakes has been demonstrated as well;⁹⁻¹¹ this type of organic film growth enhances structural order, grain size, and charge transport. However, until now, h-BN films obtained from scalable processes, such as chemical vapor deposition (CVD), have not been explored for OFET applications, raising a question as to whether h-BN can be truly suitable for low-cost, large-scale organic electronic manufacturing.

Here, we demonstrate that CVD-grown h-BN is an excellent dielectric to grow organic crystals for electronic applications, especially for OFETs. In this study, we choose C₆₀, a representative n-type organic material, as the channel material. OFETs based on C₆₀ films grown on single-layer CVD h-BN exhibit an average mobility of 1.7 cm²V⁻¹s⁻¹ and a maximum mobility of 2.9 cm²V⁻¹s⁻¹ with on/off ratios of 10⁷, showing superior OFET performance compared to that of C₆₀ grown on SiO₂/Si substrate. Our comprehensive study confirms that the epitaxial two-dimensional growth and large grain sizes of C₆₀ on CVD h-BN are mainly responsible for the enhanced charge carrier transport, proving CVD h-BN's suitability as a scalable growth template/dielectric layer. Considering CVD h-BN has numerous grain boundaries and some surface residues resulted from the transfer process, the obtained device performance can be further improved by optimization of the h-BN CVD and transfer process. Moreover, since the transfer of CVD h-BN does not require high-temperature processing, CVD h-BN will find a

variety of applications, especially in flexible electronics whose substrates require low temperatures.

Results and discussion

The large-area growth of h-BN on various metal substrates has been recently demonstrated by CVD.^{20, 21} We synthesized single-layer CVD h-BN on Pt foil and transferred it onto a SiO₂/Si substrate (See Methods for detailed synthesis and transfer process).²² The synthesized h-BN generally shows the clean surface morphology with a roughness of 0.17 nm (Supporting Figure S1) even though it shows some scattered residue resulting from the transfer process. The observed flatness of h-BN and its lack of dangling atomic can enable the growth of large C₆₀ grains on h-BN. After the preparation of h-BN template, 20-nm-thick C₆₀ was evaporated at the rate of 0.2 Å/s to form a C₆₀ film on h-BN under a vacuum pressure of 2×10⁻⁶ Torr.

The thin film structure of C₆₀ assembly on h-BN is investigated using transmission electron microscopy (TEM) imaging and selected area electron diffraction (SAED). There have been recent studies on organic molecular assembly on metal-substrate-supported h-BN by scanning tunneling microscopy.²³⁻²⁵ Even though these studies reveal that h-BN can be utilized to obtain well-organized molecular assembly by substrate-molecule interactions,²³⁻²⁵ there is no reported study on C₆₀ assembly on h-BN by any molecular imaging tool. We note that the imaging of the packing structures of C₆₀ inside boron nitride nanotubes has been performed by TEM.²⁶ In our study, a C₆₀ film assembled on suspended h-BN is investigated by adapting characterization methods similar to our previous study on C₆₀/graphene.¹³

Figure 1 shows TEM images of C_{60} crystals deposited on h-BN. A low magnification TEM image of the sample shows that C_{60} evaporated on CVD h-BN has a grain size of ~ 200 nm, which is larger than that of C_{60} on amorphous carbon (~ 50 nm) (Supporting Figure S2). This is likely due to the atomically flat nature of h-BN and molecular assembly by C_{60} /h-BN van der Waals interactions. SAED of C_{60} film on h-BN shows the single-crystal-like signal, which confirms that the grain size of C_{60} is bigger than 100 nm – the electron-beam size (Figure 1c,d). Another important feature of TEM is that it allows us to study the in-plane epitaxial alignment of C_{60} crystals on h-BN. From the acquired SAED, the relative rotational relationship between h-BN and C_{60} crystal direction can be investigated (Figure 1c,d and Supporting Figure S2). Here, the relative rotation angle Θ is defined as the angle between the first order diffraction peaks between h-BN and C_{60} in the reciprocal lattice (Figure 1c,d). Θ also represents the angle between h-BN zigzag lattice direction and the C_{60} crystal facet in real space (Figure 1b). The histogram of observed rotational angle Θ shows two strong peaks at $\Theta = 10 \pm 4^\circ$ and $\Theta = 26^\circ$. Our results suggest that there is a mild rotational alignment effect between the lattice of h-BN and the C_{60} crystallographic direction. High-resolution TEM images of C_{60} grown on CVD h-BN also clearly reveal highly-ordered local molecular assembly (Figure 1e). The C_{60} crystals on mechanically exfoliated h-BN flakes shows more pronounced epitaxy with rotational angles at $\Theta = 10 \pm 1^\circ$ and $\Theta = 26^\circ$ (Supporting Figure S3). Therefore, the somewhat broadened angular distribution on CVD h-BN, especially around at $\Theta = 10^\circ$, can be attributed to extrinsic factors such as the polycrystalline nature of CVD h-BN (the average grain size of ~ 1 micrometer) and the imperfect surface quality of CVD h-BN since these nucleation sites can induce of non-ideal epitaxial growth of C_{60} crystals.

To further understand the observed interfacial alignment, we perform first-principles density functional theory calculations including van der Waals (vdW) dispersion forces (see Methods for details). We initially considered a number of C_{60} molecular configurations towards h-BN surface and calculated their electronic and energetic structures. A computational screening taking into account the relative orientation of atoms at C_{60} molecule at apex, pentagon, hexagon, and dimer positions resulted in 12 different interface geometries with h-BN (Supporting Figure S4). The adsorption energies were computed at two different levels with and without vdW interactions (Supporting Figure S3), which strikingly show the effect of nonlocal correlations responsible for energies as high as one order of magnitude relative to non-vdW calculations. This result strongly indicates that vdW interactions play a role in the creation of the interface. Moreover, we also observed a cooperative effect from the interactions of the C_{60} molecules in the monolayer coverage of C_{60} on the h-BN surface (Supporting Figure S5). This cooperativeness is responsible for more than 16% of the calculated binding energy as compared to more dilute systems. An interaction energy at the C_{60} layer of -0.52 eV per molecule is observed, which allows further polarization of the interface and extra charge redistribution. The different bonding nature between C-C and B-N determined by their electronegativities – B(2.040), C(2.551), and N(3.041) – also provides an additional ingredient for the stabilization of the interactions.

By taking into account the different configurations of C_{60} /h-BN interface and choosing the most stable structure, we calculate the crystal-direction-dependent adhesion energies (opposite in sign to binding energies) as a function of the rotational angle Θ (Figure 1g) for the entire set of values. We use the same orientation as Figure 1b above, that is, $\Theta = 0$ and $\Theta = 30^\circ$ correspond to zigzag and armchair directions. Our vdW simulations clearly show that configurations near zigzag direction (~ 0 -2 degrees), 9-12 degrees, and 21~25 degrees have higher stability than nearby

angular orientations. Experimentally-observe epitaxy angles (Figure 1f and Supporting Figure S3) generally capture the calculated epitaxy energy landscape, in which a large population of samples with an orientation closes to $\sim 10^\circ$ are measured. We note that the expected epitaxy near 0 degree is not clearly observed in the experimental data.

The morphology of C_{60} films evaporated on CVD h-BN/SiO₂ is also investigated using atomic force microscopy (AFM) as shown in Figure 2. The topography and phase AFM images in Figures 2a and 2b show the terrace structure of C_{60} on CVD h-BN, which indicates the two-dimensional, layer-by-layer growth mode of C_{60} on h-BN. Measured step heights between C_{60} layers are ~ 0.8 nm, which is consistent with the known thickness of a single layer of C_{60} (Figure 2f). The two-dimensional growth of C_{60} on CVD h-BN is facilitated by the van der Waals interactions between C_{60} and CVD h-BN, which was also observed in TEM experiments. In contrast, C_{60} evaporated on SiO₂ shows island-shaped grains as demonstrated in Figure 2c. The apparent grain size of C_{60} on CVD h-BN is around 100~200 nm, a few times larger than that of C_{60} on SiO₂. Moreover, C_{60} on CVD h-BN has better grain connectivity and a more uniform height distribution than C_{60} on SiO₂ as depicted in Figures 2d and 2e. The better grain connectivity observed combined with the large grains of C_{60} on CVD h-BN indicates the potential for more efficient charge transport in C_{60} /h-BN/SiO₂ compared to C_{60} /SiO₂.

Grazing-incidence wide angle X-ray diffraction (GIXD) measurements provide structural information on the morphology of C_{60} that are grown on CVD h-BN on a larger area (a few hundred of micrometers). Figure 3a and 3b display the GIXD data for C_{60} on CVD h-BN and C_{60} on SiO₂, respectively. The diffraction patterns show a strong reflection on the meridian at $q_z \sim 0.76 \text{ \AA}^{-1}$, which corresponds to the (111) plane of a face-centered cubic (fcc) lattice. This indicates that the (111) faces of C_{60} fcc grains are well-aligned and parallel to CVD h-BN

surface, confirming the epitaxial growth of C_{60} mediated by van der Waals interactions. Other observed peaks are also consistent with the two-dimensional closed packed structure of C_{60} film.²⁷ On the other hand, isotropic diffraction rings in Figure 3b indicate that C_{60} fcc grains are randomly oriented on SiO_2 .

The coherence length of C_{60} crystal is calculated using the Scherrer formula²⁸ and the full width at half-maximum (FWHM) values of the $(11\bar{1})$ reflection at $q_{xy} = 0.73 \text{ \AA}^{-1}$ and $q_z = 0.24 \text{ \AA}^{-1}$. The calculated coherence length for C_{60} on CVD h-BN is $\sim 47 \text{ nm}$, whereas the coherence length of C_{60} on SiO_2 is $\sim 14 \text{ nm}$. The larger coherence length of C_{60} on h-BN as compared to that on SiO_2 confirms our TEM and AFM results.

We now discuss the electrical characteristics of OFETs based on C_{60} on CVD h-BN. Figure 4a shows a schematic of C_{60} OFET prepared on CVD h-BN. A representative transfer curve of FETs incorporating C_{60} on CVD h-BN is shown in Figure 4b. The highest observed mobility is $2.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (Figure 4b). The very high average mobility of $1.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ is achieved using C_{60} on CVD h-BN as shown in the histogram of measured mobility values in Figure 4c. Transfer curves for C_{60} on SiO_2 are given for comparison to C_{60} on CVD h-BN as shown in Figures 4d and 4e. The charge carrier mobility of C_{60} on CVD h-BN is 40 times higher compared to that of C_{60} on SiO_2 , which shows the average value of $0.04 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Since the mobility in organic field-effect transistors is very sensitive to the surface roughness and traps on a dielectric layer, the high mobility suggests that CVD h-BN is an excellent dielectric and growth template for C_{60} .

We emphasize that this is the first demonstration of organic semiconductor growth and device fabrication on large-area CVD h-BN. Previously, various surface treatments of dielectric substrate, such as functionalization by self-assembled molecular layer, have been utilized to

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3 improve the morphology/grain size of deposited C₆₀ crystals and related device performance.²⁹⁻³²

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5 The best reported mobility values of C₆₀ transistors on these functionalized surfaces range from 2
6 to 5 cm²V⁻¹s⁻¹, where the highest value (~10 cm²V⁻¹s⁻¹) was obtained with solution-processed
7 isolated C₆₀ single crystals.²⁹⁻³² When we consider C₆₀ transistors composed of fully-covered C₆₀
8 film, the observed maximum mobility value of 2.9 cm²V⁻¹s⁻¹ using CVD h-BN is comparable to
9 the highest reported mobility values. Currently, the CVD synthesis process for h-BN is not as
10 optimized as that for graphene, and thus the grown h-BN layer has smaller grain sizes (the
11 average grain size of ~ 1 micrometer) and a noticeable density of residues, resulting in the
12 hysteresis in the transistor operation (Supporting Figure S6). The device performance is expected
13 to improve further as the h-BN synthesis and transfer processes are optimized.
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31 Conclusion

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34 In conclusion, we demonstrate that CVD h-BN is an excellent dielectric layer for C₆₀ deposition
35 and FET applications. The epitaxial relationship between C₆₀ and h-BN is studied in detail using
36 TEM characterization and first-principles calculations. The large sizes and crystal orientation of
37 C₆₀ grains on CVD h-BN are investigated with AFM and GIXD. Furthermore, we report high-
38 performance field-effect transistors based on C₆₀ on CVD h-BN. The high mobility values
39 reaching 2.9 cm²V⁻¹s⁻¹ suggest that CVD h-BN is a promising dielectric for organic
40 semiconductor devices. Given its low temperature requirements, CVD h-BN is expected to find
41 more general use for flexible devices that require low temperature process.
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Methods

h-BN Synthesis and Transfer. h-BN was synthesized using chemical vapor deposition.²²

Ammonia borane was heated at 130°C to be decomposed into borazine, hydrogen, and polyiminoborane. The borazine and hydrogen gas was flowed onto Pt foil in a furnace at 1100°C. Then, borazine is decomposed and forms single layer h-BN on the Pt foil. For the transfer process, PMMA was spin coated onto the h-BN/Pt foil and cured. The PMMA/h-BN/Pt foil was dipped into a 1M aqueous solution of NaOH and used as the cathode of an electrolysis cell. The water reduction at the cathode generates H₂ bubbles between PMMA/h-BN and the Pt foil, which then detach the PMMA/h-BN from the Pt foil. The separated PMMA/h-BN was then transferred onto 300 nm SiO₂/Si substrates for transistor fabrication. After the transfer, PMMA was removed in acetone, and then residual PMMA was further removed by heating at 400°C for 2h under H₂/Ar atmosphere. For comparison study, BN powders from Momentive Performance Materials were mechanically exfoliated to produce thin h-BN flakes on SiO₂/Si wafer. The samples were calcinated at 450°C for 1 hour to remove possible tape residue on the surface of h-BN flakes. For preparation of TEM grids with CVD h-BN, PMMA-covered CVD h-BN was transferred onto Quantifoil holey carbon TEM grids and PMMA was removed in acetone. In the case of mechanically exfoliated h-BN samples, the flakes on SiO₂/Si wafer were transferred to TEM grids by the direct transfer method.³³

C₆₀ Film Preparation and Au Evaporation. Before C₆₀ evaporation, TEM grids with CVD h-BN were pre-annealed in air at 200°C for 30 min to minimize the possible adsorbates on the h-BN surface. After the pre-annealing process, TEM grids were attached onto the evaporator substrate with Kapton tape. 300-nm SiO₂/Si substrates were also fixed onto the evaporator substrate for device fabrication. 20-nm-thick C₆₀ films were thermally evaporated on both h-

BN/TEM grids and device substrates at the substrate temperature of 110 °C with an evaporation rate of $0.2 \text{ \AA s}^{-1}$. Au electrodes (40 nm thick) were thermally evaporated through a shadow mask with a channel length and width of 50 μm and 1000 μm respectively.

TEM Characterizations. TEM imaging and selected area electron diffraction (SAED) acquisition were performed with a FEI Titan Cube G2 60-300 operated at 80 kV with an image aberration corrector. Extra SAED acquisition was performed using a JEOL 2100F, which is operated at 200 kV.

GIXD Characterization. GIXD images were collected in reflection mode with a 2-D area detector (MAR-345; pixel size of 150 μm , $2,300 \times 2,300$ pixels) and the sample in a helium atmosphere at beamline 11-3 of the Stanford Synchrotron Radiation Lightsource. The sample to detector distance was 400 mm, which was calibrated using a LaB_6 polycrystalline standard. The incidence angle was 0.12° . The X-ray wavelength was 0.9758 $\text{\AA}$, corresponding to a beam energy of 12.7 keV. Before performing quantitative analysis on the images, the data was corrected for the theta-dependent image distortion caused by the planar detector surface. Numerical integration of the diffraction peak areas was performed with the software WxDiff. The overall resolution in the GIXD experiments was about $0.01 \text{ \AA}^{-1}$.

Electrical Characterization. The device measurement was performed inside a nitrogen glove box using a Keithley 4200-SCS semiconductor parameter analyzer. The saturation mobility was extracted from the slope of the transfer curve of $I_{\text{DS}}-V_{\text{GS}}$, using $I_{\text{DS}} = \mu W C_{\text{ox}} (V_{\text{G}} - V_{\text{T}})^2 / 2L$, where μ is the mobility, W is the channel width, L is the channel length, C_{ox} is the gate capacitance per unit area, and V_{T} is the threshold voltage.

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Theoretical Calculations. Calculations were based on *ab initio* density functional theory using the SIESTA method³⁴ and the VASP code.^{35, 36} The generalized gradient approximation³⁷ along with the DRSLL^{38, 39} functional was used in both methods, together with a double- ζ polarized basis set in SIESTA, and a well-converged plane-wave cutoff of 500 eV in VASP. We used a Fermi-Dirac distribution with an electronic temperature of $k_B T = 20$ meV. Additional details are provided in the Supporting Information.

Figure 1. Orientation alignment of C_{60} crystals on CVD h-BN membrane. (a) A schematic side-view of C_{60} film on h-BN membrane. (b) Top-view of C_{60} crystal on h-BN. The relative angle Θ between h-BN zigzag lattice direction and C_{60} crystal facet is used for labelling epitaxial alignment. (c,d) Selected area electron diffraction of C_{60} film on h-BN. The single-crystal-like C_{60} diffractions are observed. (e) High-resolution TEM image of C_{60} crystal prepared on h-BN. The marked circle indicates the size and location of C_{60} molecule. Scale bar, 2 nm. (f) Histogram of observed relative rotational angle of C_{60} crystal on h-BN. (g) Calculated orientation-dependent adhesion energy (opposite sign to binding energies) of C_{60} on h-BN. Colored regions indicate stable configurations with local maximum adhesion energy.

Figure 2. Two-dimensional growth of C_{60} on CVD h-BN. (a) AFM height and (b) phase images for C_{60} on CVD h-BN. Clear terrace structure and large C_{60} grains are observed. Scale bar, 250 nm. (c) AFM height image for C_{60} on SiO_2 . C_{60} on SiO_2 has a small grain size and no terrace structure. Scale bar, 250 nm. (d) Comparison of AFM cross-section images for C_{60} on h-BN and C_{60} on SiO_2 along marked yellow lines. Height profile for C_{60} on h-BN is more uniform than that for C_{60} on SiO_2 . (e) Histogram of the height distribution. (f) Step heights between C_{60} layers. Observed step heights are around 0.8 nm, which is consistent with the known C_{60} single-layer thickness value.

Figure 3. Well-ordered C₆₀ grains on CVD h-BN compared to C₆₀ on SiO₂. (a) GIXD measurement data for C₆₀ on CVD h-BN. The diffraction peaks on the meridian at $q_z = 0.76 \text{ Å}^{-1}$ show that (111) planes of the C₆₀ face-centered-cubic crystals are well-ordered and parallel to the h-BN surface. (b) GIXD measurement for C₆₀ on SiO₂. The ring shaped diffraction patterns indicates that C₆₀ grains on SiO₂ are randomly oriented in all directions. (c) C₆₀ packing structure on h-BN. (d) C₆₀ packing structure on SiO₂.

Figure 4. Electrical characteristics of C₆₀ FETs on CVD h-BN. (a) Schematics of C₆₀ FET on CVD h-BN. (b) Transfer curve of C₆₀ FETs on h-BN with the maximum mobility of 2.9 cm²V⁻¹s⁻¹. (c) Histogram of electron mobility measured in C₆₀ FETs on h-BN. The average mobility is around 1.7 cm²V⁻¹s⁻¹. (d,e) Comparison of transfer curves from C₆₀ FETs on h-BN vs. on SiO₂. Panel d shows the $I_{DS}^{1/2}$ data on a linear scale. Panel e shows the I_{DS} data on a semi-log scale.

ASSOCIATED CONTENT

Supporting Information. Additional adsorption energy calculations of C₆₀ on h-BN with detailed calculation methods, additional AFM and TEM images of samples, TEM data on C₆₀ epitaxy on mechanically exfoliated h-BN flakes, and output curves of C₆₀/h-BN devices. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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TOC Graphic

34x14mm (300 x 300 DPI)