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# Synthesis of large single-crystal hexagonal boron nitride grains on Cu-Ni alloy

Guangyuan Lu<sup>1,\*</sup>, Tianru Wu<sup>1,\*</sup>, Qinghong Yuan<sup>2</sup>, Huishan Wang<sup>1,3</sup>, Haomin Wang<sup>1</sup>, Feng Ding<sup>4</sup>, Xiaoming Xie<sup>1,5</sup> & Mianheng Jiang<sup>1,5</sup>

Hexagonal boron nitride (h-BN) has attracted significant attention because of its superior properties as well as its potential as an ideal dielectric layer for graphene-based devices. The h-BN films obtained via chemical vapour deposition in earlier reports are always polycrystalline with small grains because of high nucleation density on substrates. Here we report the successful synthesis of large single-crystal h-BN grains on rational designed Cu-Ni alloy foils. It is found that the nucleation density can be greatly reduced to 60 per mm<sup>2</sup> by optimizing Ni ratio in substrates. The strategy enables the growth of single-crystal h-BN grains up to 7,500 μm<sup>2</sup>, approximately two orders larger than that in previous reports. This work not only provides valuable information for understanding h-BN nucleation and growth mechanisms, but also gives an effective alternative to exfoliated h-BN as a high-quality dielectric layer for large-scale nanoelectronic applications.

<sup>1</sup>State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, 865 Changning Road, Shanghai 200050, China. <sup>2</sup>Department of Physics, East China Normal University, Shanghai 200241, China. <sup>3</sup>School of Physics and Electronics, Central South University, Changsha 410083, China. <sup>4</sup>Institute of Textiles and Clothing, Hong Kong Polytechnic University, Kowloon, Hong Kong 999077, China. <sup>5</sup>School of Physical Science and Technology, Shanghai Tech University, 319 Yueyang Road, Shanghai 200031, China. \* These authors contributed equally to this work. Correspondence and requests for materials should be addressed to X.X. (email: xmxie@mail.sim.ac.cn).

Hexagonal boron nitride (h-BN) is a representative two-dimensional (2D) crystal with a band gap of  $\sim 6$  eV (ref. 1). Owing to the strong covalent  $sp^2$  bonds in the plane, it has very high mechanical strength, thermal conductivity and chemical stability<sup>2–6</sup>. The h-BN layer with atomically smooth surface free of dangling bonds/charge traps makes it an ideal dielectric substrate for field effect transistor<sup>7</sup> and spacer for novel tunnelling devices<sup>8,9</sup>. The characters of h-BN make it possible to realize ballistic electronics at room temperature<sup>10,11</sup>. Normally, uniform crystalline h-BN flakes are mostly obtained by mechanical exfoliation from h-BN single crystals<sup>7,11–15</sup>. However, the flakes are obtained through a highly skilled manual process—mechanical exfoliation and transferring, which is not a scalable method for practical applications. So far, many efforts have been taken on various substrates such as Ni<sup>16–21</sup>, Cu<sup>3,21–27</sup>, Pt<sup>28,29</sup>, Ru<sup>30,31</sup> and Co<sup>32</sup> to obtain large h-BN crystals via the chemical vapour deposition (CVD) process. However, those grains in h-BN films are very small (usually  $< 50 \mu\text{m}^2$ ) because of high nucleation density at the early growth stages<sup>10,11,15–17,19,22</sup>. The small grains lead to high density of grain boundaries and dangling bonds, which are known as structural defects in h-BN<sup>33,34</sup>. The defects definitely give rise to higher surface roughness/charge impurities, and then degrade the performance of electronic devices<sup>35</sup>. Therefore, the growth of high-quality, large h-BN crystals is essential in the commercial-level manufacture for its further application in electronic, photonic and mechanical devices.

Here we report the successful synthesis of large-size single-crystal h-BN grains on rationally designed binary Cu–Ni alloy. It is observed that under our growth conditions the nucleation density can be dramatically decreased by introducing Ni to the Cu substrate. Ten to twenty atom % of Ni can reduce the nucleation density down to  $60 \text{ mm}^2$ , and h-BN grains of  $\sim 7,500 \mu\text{m}^2$  in area can be obtained. The grains are about two orders larger than those in previous reports<sup>10,11,15–17,19,22</sup>. The introduction of Ni is also proved to enhance the decomposition of poly-aminoborane and help synthesize high-quality h-BN grains free of nanoparticles. The characterizations such as Auger electron spectroscopy (AES), atomic force microscopy (AFM) and transmission electron microscopy (TEM) confirm that h-BN grains are uniform. Our results demonstrate that the CVD-grown h-BN layer with large grain can help effectively preserve the intrinsic properties of graphene, and will certainly facilitate the further application of wafer-scale electronics.

## Results

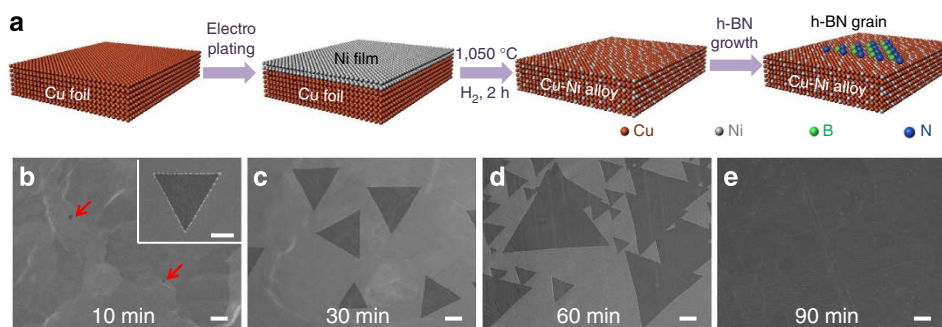
**h-BN growth.** In our work, Cu–Ni alloy was used as the catalytic substrate for h-BN growth. The alloy was obtained by annealing

Ni-coated Cu foils at  $1,050^\circ\text{C}$  for 2 h in flowing hydrogen. Ammonia borane ( $\text{H}_3\text{BNH}_3$ , also called borazane) was supplied as the precursor for h-BN growth. By heating the precursor to  $70\text{--}90^\circ\text{C}$ , borazane began to dissociate and the products were carried into the reaction chamber in a  $\text{H}_2$  flow at a pressure of  $\sim 50$  Pa. The growth temperature was  $\sim 1,050^\circ\text{C}$ . The schematic of process flow is illustrated in Fig. 1a, and the experimental details are given in Supplementary Fig. 1.

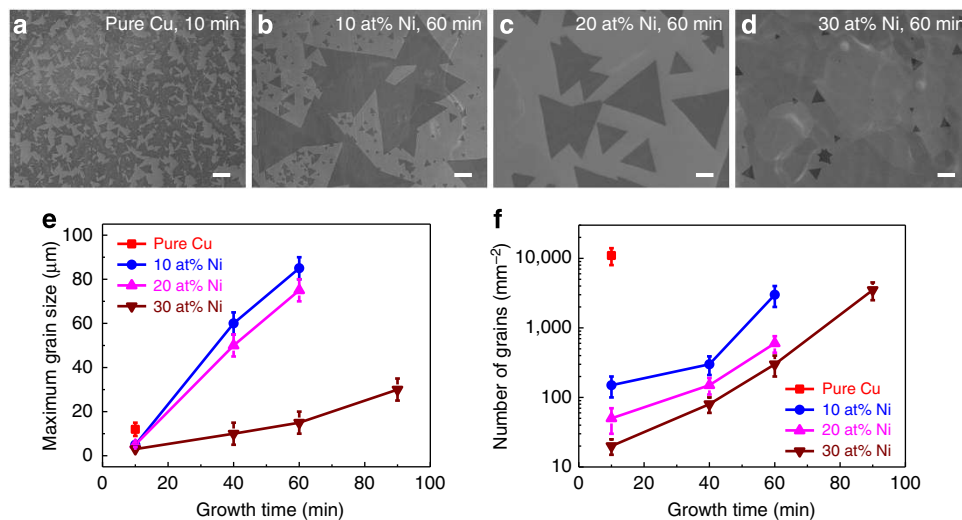
Figure 1b–e shows the scanning electron microscopy (SEM) images of h-BN grown at  $1,085^\circ\text{C}$  on Cu–Ni alloy substrates with 15 atom % Ni. It can be clearly seen that the h-BN grains nucleate, grow up and finally coalesce into a continuous film. The typical lengths of side for triangle h-BN grains after 10 and 40 min of growth were 5 and  $60 \mu\text{m}$ , respectively, while grains with the length of side up to  $130 \mu\text{m}$  were obtained after 60 min. All the h-BN grains obtained are in triangular shape (Fig. 1b–d), which implies that these grains are all single crystals with nitrogen-terminated zigzag edges<sup>16,17,23</sup>. h-BN grains growing across alloy grain boundaries are also frequently observed, suggesting that under the conditions h-BN growth is surface-mediated<sup>23</sup>.

Experiments were carried out to understand the influence of Ni concentration on h-BN growth. Figure 2a shows a typical SEM image of h-BN grains grown on pure Cu foil for 10 min at  $1,050^\circ\text{C}$ . It could be observed that the nucleation density of the h-BN grains is so high that the triangular-shaped grains with only  $\sim 10\text{--}15 \mu\text{m}$  in the length of side are about to coalesce. Figure 2b–d shows SEM images of h-BN grains grown for 60 min on Cu–Ni alloy foils with 10, 20 and 30 atom % Ni, respectively. And the relationship between the largest grain size and growth time is given in Fig. 2e, while the relationship between the number of grains and growth time is shown in Fig. 2f. It can be found that the nucleation density decreased notably after introducing Ni element. On Cu–Ni alloy substrate with 10–20 atom % Ni, the largest length of side for single-crystal h-BN grains reaches  $\sim 70\text{--}90 \mu\text{m}$  with a lateral growth rate of  $\sim 1.2 \mu\text{m min}^{-1}$ . The nucleation density dropped further on 30 atom % Ni substrates, but the lateral growth rate dropped to  $\sim 0.3 \mu\text{m min}^{-1}$ , with the largest length of side for grains only achieved  $\sim 30 \mu\text{m}$ . The same experiments were also taken on Ni foils and Cu–Ni alloy foils with 50 atom % Ni; however, in the present process window, h-BN grains were not observed even after 90 min of growth for both cases (see Supplementary Fig. 2).

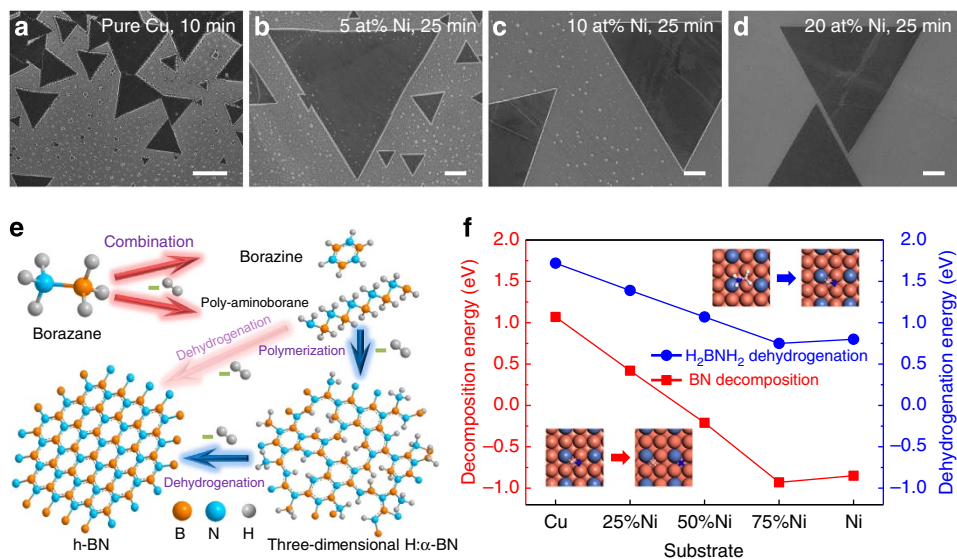
The growth mechanism of h-BN on Cu is mainly surface-mediated<sup>23,25</sup>, while on Ni, it is neither surface-limited nor dominated by segregation and precipitation of B and N, but rather depends on surface chemistry of Ni–B and Ni–N<sup>18</sup>. Our experimental parameters of h-BN growth on Cu–Ni substrate



**Figure 1 | Rational design of Cu–Ni alloy substrates for h-BN growth.** (a) Schematic illustration showing the procedure of h-BN growth. (b–e) Typical SEM images of h-BN grains grown on Cu–Ni alloy foils with 15 atom % Ni at  $1,085^\circ\text{C}$  for 10, 30, 60 and 90 min, respectively. The red arrows in **b** show the sites of the h-BN grains, while the inset shows the enlarged image of one as-grown h-BN grain. The scale bars in **b–e** are  $20 \mu\text{m}$ , and in inset in **b** is  $2 \mu\text{m}$ .



**Figure 2 | Effect of Ni concentration on the maximum grain size and the number of grains.** (a) SEM images of h-BN grains grown on Cu foil for 10 min at 1,050 °C. (b–d) SEM images of h-BN grains grown for 60 min on Cu–Ni alloy foils with (b) 10 atom %, (c) 20 atom % and (d) 30 atom % Ni at 1,050 °C. The scale bars are 20 μm in a–d. (e) Dependence of the maximum h-BN grain size on Ni concentration and growth time. (f) Dependence of the number of h-BN grains on Ni concentration and growth time.



**Figure 3 | Enhancing the dissociation of borazane oligomers by introducing Ni.** (a) SEM images showing the morphology of a Cu foil after the growth of h-BN for 10 min at 1,050 °C. (b–d) SEM images of Cu–Ni alloy foils with (b) 5 atom %, (c) 10 atom % and (d) 20 atom % Ni after growth of h-BN for 25 min at 1,050 °C. (e) Schematic diagram showing the structural development from dissociation of borazane to h-BN. (f) The molecular dynamic simulation of H<sub>2</sub>BNH<sub>2</sub> dissociation on the surface of different substrates. The scale bars in a–d are 5 μm.

with 10–20 atom % Ni are based on the surface-mediated mechanism on Cu foils. With further increase in Ni content, new growth mechanism based on solid-gas reactions involving Ni–B and Ni–N sets in, so that the growth of h-BN would move entirely to a different process window, accounting for decreased growth rate or even inability for phase formation.

As shown in Figs 1b–d and 2e,f, it is also discovered that nucleation continued with its rate increased nonlinearly with time, while the early nuclei developed in size during growth. Similar phenomenon has also been reported for h-BN growth on Cu foils<sup>23</sup>. It is therefore clear that the key to success for large grain size is to reduce the initial nucleation density and to suppress the continuous nucleation during growth.

**Mechanisms.** Figure 3a–d compares the typical surface morphologies of h-BN grown on Cu (10 min at 1,050 °C) and Cu–Ni alloys (25 min at 1,050 °C, 5–20 atom % Ni). Many nanoparticles (appearing white in SEM) are observed on Cu surface, while the density decreases dramatically with the increasing of Ni concentration in substrates. The nanoparticles disperse randomly among h-BN grains or accumulate along its perimeters, and are statically correlated to the h-BN grain nucleation (see Supplementary Fig. 3).

As illustrated in Fig. 3e, the borazane precursor (H<sub>3</sub>BNH<sub>3</sub>) decomposes into gaseous borazine (B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>) and solid poly-aminoborane (BH<sub>2</sub>NH<sub>2</sub>)<sub>n</sub> upon heating to 70–90 °C (refs 23,24,36–40). Poly-aminoborane can hardly develop into h-BN unless a very high temperature of 1,170–1,500 °C is applied if

without catalytic substrates<sup>40</sup>. Previous studies indicate that on catalytic surface the resulting polymer undergoes a two-stage weight loss process: 2D cross-linking reaction of B-H and N-H groups is initiated from 125 to 200 °C, and then dehydrogenation from unaligned chain branches continues from 600 to 1,100 °C (refs 20,36). The reactions involved suggest that the nanoparticles are most likely a complex mixture of poly-aminoborane and its partially dehydrogenated derivatives, consistent with earlier reports<sup>23,24,26,41</sup> and our Auger investigations (Supplementary Fig. 3a–e).

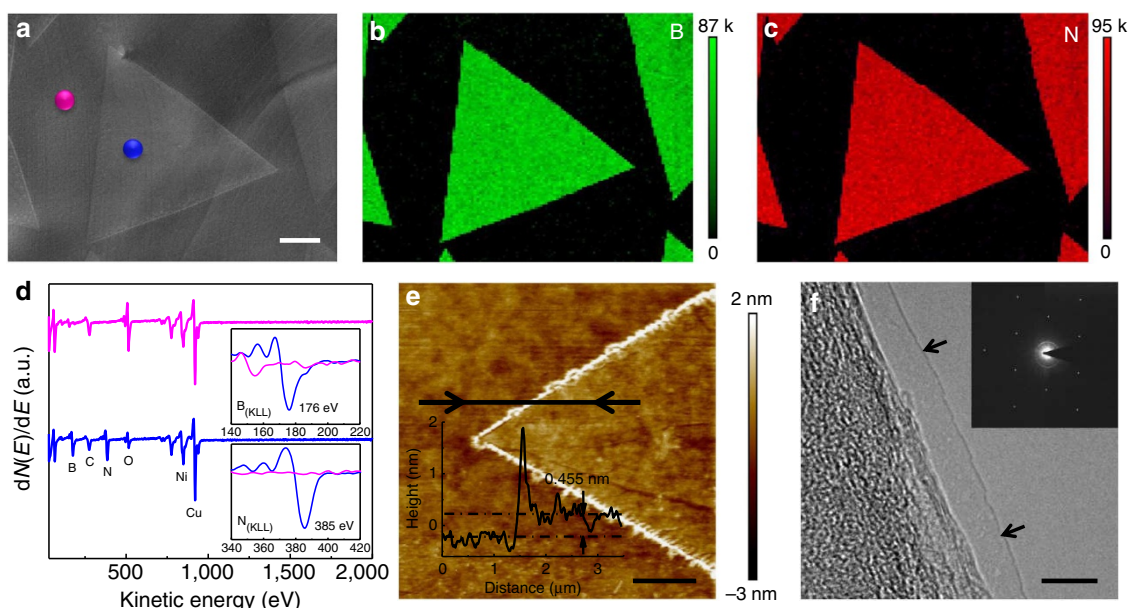
To have a better understanding on the suppressed formation of nanoparticles at higher Ni content, we carried out simplified density functional theory (DFT) calculations of decomposition energy of  $(\text{BH}_2\text{NH}_2)_{n=1}$  on substrates with different compositions (Fig. 3f, details of the calculations are given in Supplementary Fig. 4). The calculation shows that dehydrogenation of  $\text{BH}_2\text{NH}_2$  becomes easier by increasing the Ni content in our alloy substrates in a certain range. On the other hand, the decomposition energy of BN, dehydrogenated derivative of  $\text{BH}_2\text{NH}_2$ , drops more evidently by introducing Ni to the Cu substrate. It is apparent that the introduction of Ni can enhance the decomposition of poly-aminoborane, which helps the reactions of desorption or the formation of Ni–B and Ni–N phases<sup>18</sup>, consistent with the weak h-BN growth on Cu–Ni alloy with 30 atom % Ni. To enable growth of h-BN on Cu–Ni alloy with high Ni content, one would have to increase the precursor supply; thus, the growth of h-BN enters into a completely different process window<sup>18,19,21,23,24</sup>.

**Characterization.** Figure 4a–c shows the SEM image and the corresponding B(KLL) and N(KLL) Auger electron maps of a typical h-BN grain grown on Cu–Ni alloy foil with 15 atom % Ni. It is found that distributions of B and N elements are homogeneous in the grains. Figure 4d presents the AES spectra taken in the blue and magenta dotted areas shown in Fig. 4a, while the insets show the corresponding B(KLL) and N(KLL) spectra, respectively.

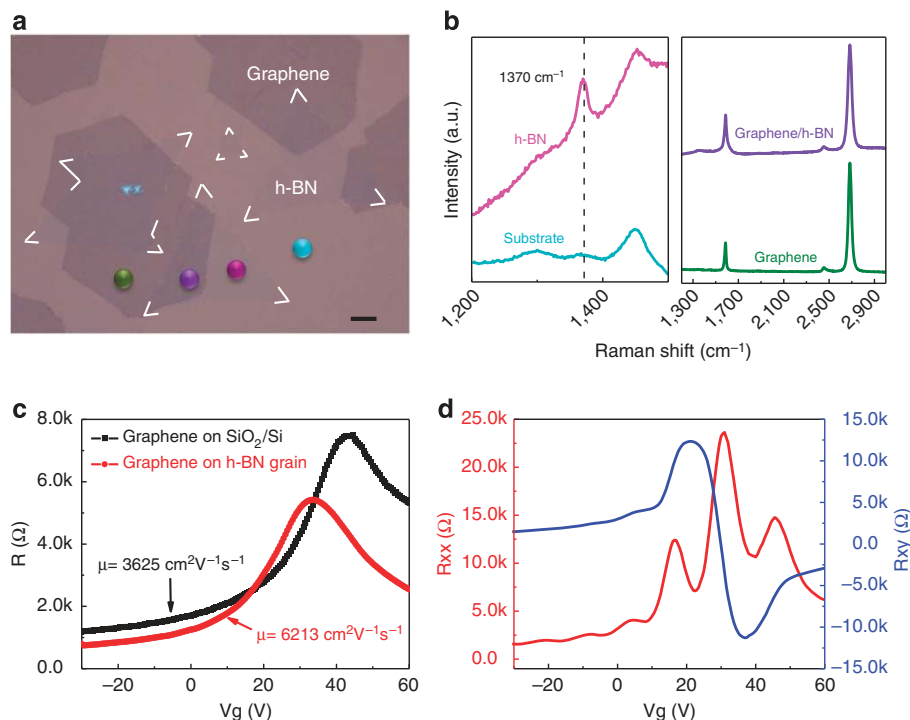
The B(KLL) and N(KLL) peaks measured on h-BN grain are at 176 and 385 eV, respectively, in agreement with those given in previous reports<sup>42,43</sup>. It can also be seen that the BN-coated area (blue dot) shows a much weaker peak of O(KLL) than the uncoated area (magenta dot), proving the high oxidation resistance of the h-BN film<sup>44</sup>. Besides homogeneous h-BN grains, some triangular-shaped h-BN ad-layers with size of more than 10  $\mu\text{m}$  were occasionally observed (Supplementary Fig. 5). The edges of the ad-layers are parallel to those of the first layer, implying strict stacking orders of the h-BN multilayers.

Figure 4e shows the AFM image of a corner of a triangular-shaped h-BN grain transferred on the  $\text{SiO}_2/\text{Si}$  substrate. The height of the transferred film is  $\sim 0.455$  nm, consistent with that reported for single-layer h-BN<sup>23,24,28,29</sup>. Figure 4f shows a typical TEM image obtained at the edge of the h-BN film on a TEM grid, confirming that the h-BN prepared is monolayered. The selected area electron diffraction pattern presented in the inset of Fig. 4f shows a set of characteristic sixfold symmetric spots, indicating that the h-BN grain is well crystallized. TEM images containing two to four atomic layers were also occasionally detected, as shown in Supplementary Fig. 6. More characterizations of the h-BN grains, including X-ray photoemission spectroscopy (XPS), optical image and optical absorption spectrum are presented in Supplementary Fig. 7.

**Application.** We fabricated graphene/h-BN heterostructure to evaluate the quality of CVD-grown h-BN (the transferring method is given in Supplementary Fig. 8). Figure 5a shows the optical image of graphene/h-BN heterostructure on a 90-nm  $\text{SiO}_2/\text{Si}$  substrate, with the Raman spectra taken in different areas presented in Fig. 5b. The spectrum taken in the surface of h-BN (magenta dot) exhibits a characteristic peak at  $1,370\text{ cm}^{-1}$  because of the  $E_{2g}$  phonon mode of h-BN<sup>45</sup>, consistent with previous report on the Raman signature of mechanical exfoliated monolayer h-BN films<sup>13</sup>. The peak near  $1,450\text{ cm}^{-1}$  is from the third-order transverse optic mode of the silicon



**Figure 4 | Characterization of h-BN grains.** (a) SEM image of a typical h-BN grain grown on a Cu–Ni alloy foil. (b,c) The corresponding B(KLL) and N(KLL) Auger electron maps, respectively. (d) AES spectra taken in the dotted areas shown in a. The insets show the corresponding B(KLL) and N(KLL) spectra, respectively. (e) AFM image of a corner of a h-BN grain transferred on the  $\text{SiO}_2/\text{Si}$  substrate. The inset shows the height distribution along the black line in e. (f) High-resolution transmission electron microscopy image of h-BN film on TEM grid with the black arrows showing that it is of monolayer thickness. The inset shows the corresponding selected area electron diffraction pattern. Scale bars are (a) 10  $\mu\text{m}$ , (e) 1  $\mu\text{m}$  and (f) 5 nm.



**Figure 5 | Characterization of graphene/h-BN heterostructure.** (a) Optical image of graphene/h-BN grains on a 90-nm SiO<sub>2</sub>/Si substrate. (b) Raman spectra taken from the dotted areas shown in **a**. (c) Resistivity of graphene/SiO<sub>2</sub>/Si and graphene/h-BN Hall bar devices versus the back-gate voltage at room temperature, respectively. The values of the extracted carrier mobility are indicated in insets. (d) Graphene/h-BN Hall device exhibits half-integer quantum Hall effect measured at 4K under a magnetic field  $B=9$  T. The scale bar in **a** is 10  $\mu$ m.

substrate<sup>46,47</sup>. Both the spectra taken in the surfaces of graphene/SiO<sub>2</sub> (olive dot) and graphene/h-BN (violet dot) indicate that the graphene grain is a well-crystallized monolayer with few defects<sup>48,49</sup>.

Graphene/h-BN and contrastive graphene/SiO<sub>2</sub>/Si Hall devices were then made to further characterize the electronic properties. Figure 5c displays the resistivity curves of typical graphene/h-BN and graphene/SiO<sub>2</sub>/Si back-gate field-effect transistors, with the calculated mobility read 6,213 and 3,625 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, respectively. The effectiveness of the CVD-grown h-BN as dielectric substrate for graphene devices is thus well proved. Moreover, as given in Fig. 5d, through the graphene/h-BN Hall device the half-integer quantum Hall effect is also observed, further confirming the high quality of both h-BN and graphene grains. As continuous h-BN films containing more than one atomic layers were synthesized and used as substrates, the mobility of our CVD-grown graphene is further improved to  $\sim 10,000$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> (see Supplementary Fig. 9).

## Discussion

In summary, we successfully grow uniform large single-crystal h-BN grains via the CVD method. By rationally designing the Cu-Ni alloy substrate, the nucleation density of h-BN can be greatly decreased to 60 per mm<sup>2</sup>. Single-crystal h-BN grains with 7,500  $\mu$ m<sup>2</sup> are obtained, which are two orders larger in area than previous reports. Characterizations such as AES, AFM and TEM confirm the uniformity of h-BN grains. Electrical transport measurements show that the CVD-grown h-BN layers exhibit excellent dielectric performance. The success brings in hope in the successive CVD growth of high-quality h-BN, as well as fabrication of graphene/h-BN heterostructure or super lattices, which are important for both fundamental research as well as device applications.

## Methods

**Deposition of Ni film on a Cu foil.** An 8 cm  $\times$  8 cm Cu foil (25  $\mu$ m, 99.8%, Alfa-Aesar) was first electrochemically polished to reduce the surface roughness. The polishing solution consisted of 500 ml of water, 250 ml of ethanol, 250 ml of orthophosphoric acid, 50 ml of isopropyl alcohol and 5 g of urea. After 90 s of electrochemical polishing with the current set at 10A, the thickness of the Cu foil reduced to  $\sim 20$   $\mu$ m. Then, the polished Cu foil was loaded into an annealing tube and annealed at 1,050  $^{\circ}$ C for 2 h in a mixed Ar/H<sub>2</sub> (400/100 sccm) flow under atmospheric pressure to further increase its surface flatness and grain size.

After annealing, the Cu foil was electroplated with a layer of Ni. The electrolytic solution was a mixture of 1 l of water, 280 g of NiSO<sub>4</sub>  $\cdot$  6 H<sub>2</sub>O, 8 g of NiCl<sub>2</sub>  $\cdot$  6 H<sub>2</sub>O, 4 g of NaF and 30 g of H<sub>3</sub>BO<sub>3</sub>. With the current density set at 0.01 A cm<sup>-2</sup>, a Ni film with a certain thickness was deposited on the Cu foil at a rate of 200 nm min<sup>-1</sup>.

**Growth of h-BN grains.** The Ni-coated Cu foils were loaded into a 5-cm diameter CVD-fused quartz tube as shown in Supplementary Fig. 1a. The distance between precursor and substrates is  $\sim 60$  cm. The annealing and growth process is shown in Supplementary Fig. 1b. The substrates were first heated to 1,050  $^{\circ}$ C and maintained for 2 h in a H<sub>2</sub> flow at a total pressure of  $\sim 5$  kPa. After that, the two metals were completely interdiffused to Cu-Ni alloy foils, with the atomic proportions determined by the thickness of the deposited Ni film before annealing. For h-BN growth, the temperature was changed to the specified value in the range of 1,050–1,090  $^{\circ}$ C, and the total pressure was maintained at 50 Pa. At the same time, borazane precursor placed in an Al<sub>2</sub>O<sub>3</sub> boat was heated to 70–90  $^{\circ}$ C by a heating lamp. After growth, both the heating furnace and the heating lamp were quickly cooled down to room temperature.

**Characterizations.** h-BN grains were characterized by SEM (Zeiss Supra55, operated at 3 kV), AES (PHI670, operated at 10 kV), AFM (Bruker Dimension Icon, contact mode), TEM (FEI Tecnai G2, 200 kV), Raman spectroscopy (Renishaw, 514 nm laser wavelength), XPS (AXIS UltraDLD) and UV-vis spectrophotometer (EV300).

**DFT calculation.** All the calculations are performed within the framework of DFT as implemented in the Vienna *Ab initio* Simulation Package. Electronic exchange and correlation are included through the generalized gradient approximation in the Perdew–Burke–Ernzerhof form. The interaction between valence electrons and ion

cores is described by the projected augmented wave method and the energy cutoff for the plane wave functions is 400 eV. All structures were optimized until the maximum force component on each atom is less than  $0.02 \text{ eV } \text{Å}^{-1}$ . The vacuum layer inside the super cell is kept as large as  $14 \text{ Å}$  to avoid the interaction of the adjacent unit cell. The slab model is composed of  $4 \times 4$  repeating unit cells and the  $2 \times 2 \times 1$  k-point mesh is used for the calculation.

The dehydrogenation energies,  $E_{\text{dh}}$ , of each dehydrogenated borazane on the surfaces are calculated by  $E_{\text{dh}} = E(\text{Sub-BN}) + 2 \times E(\text{H}_2) - E(\text{Sub}) - E(\text{H}_2\text{BNH}_2)$ , in which  $E(\text{Sub-BN})$  is the total energy of fully dehydrogenated borazane adsorbed on the substrate;  $E(\text{Sub})$  and  $E(\text{H}_2\text{BNH}_2)$  are the energies of substrate and separated  $\text{H}_2\text{BNH}_2$ , respectively;  $E(\text{H}_2)$  is the energy of hydrogen molecule in the vacuum. The decomposition energies are calculated by  $E_{\text{dc}} = E(\text{Sub-B-N}) - E(\text{Sub-BN})$ , in which  $E(\text{Sub-B-N})$  and  $E(\text{Sub-BN})$  are the energies of separated B, N atoms adsorbed on the substrate and BN cluster adsorbed on the substrate, respectively.

**Fabrication and measurement of graphene Hall devices.** CVD-grown monolayer graphene grains with a typical size of  $50 \mu\text{m}$  were transferred on as-grown h-BN grains on Cu–Ni alloy, followed by the etching of Cu–Ni and then the graphene/h-BN grains were transferred on a highly doped p-type silicon wafer with a 300-nm  $\text{SiO}_2$ -capping layer. For comparison, some graphene grains were transferred directly on the  $\text{SiO}_2/\text{Si}$  substrate. After that, a standard electron beam lithography technique was employed to pattern the Hall bar structure. The contact electrodes (10 nm Au/50 nm Ti) were deposited through electron beam evaporation. Both electrical transport and magnetotransport measurements were carried out in a PPMs-9 T system from Quantum Design.

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### Author contributions

M.J. and X.X. supervised the research work. T.W. conceived the project. T.W. and G.L. designed the experiments. G.L. performed h-BN growth, transfer and characterization. F.D. and Q.Y. performed the DFT calculations. H.W. and H.W. fabricated the graphene electronic devices and carried out the transport measurements. T.W., X.X. and G.L. analysed the experimental data and designed the figures. H.W., G.L., T.W., X.X. and M.J. co-wrote the manuscript and all authors contributed to the critical discussions of the manuscript.

### Additional information

**Supplementary Information** accompanies this paper at <http://www.nature.com/naturecommunications>

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