Orientation-controlled growth of hexagonal boron nitride monolayers templated from graphene edges

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The crystal orientation of epitaxially grown hexagonal boron nitride (hBN) monolayers from graphene edges was investigated. Low-energy electron microscopy observations reveal that the orientation of individual hBN grains is dependent on the direction of the templated zigzag edges of graphene. Furthermore, the triangular atomic defects in hBN were used to confirm the orientation of epitaxial hBN through high-resolution transmission electron microscopy observations. The results indicate that the orientation of epitaxially grown hBN is determined by the formation of carbon–boron bonds at the graphene/hBN interface, which provides a promising way of producing uniform interface structures and orientation-controlled hBN grains. © 2017 The Japan Society of Applied Physics

n-plane heterostructures of graphene and hexagonal boron nitride (hBN) monolayers have attracted much attention owing to their unique interface-originating properties and their potential applications in next-generation electronics. For example, theoretical studies have predicted many unique properties such as localized border states and ferromagnetism in graphene/hBN in-plane heterostructures.¹⁻⁴ The nanoribbons of such heterostructures are also predicted to exhibit a semimetallic behavior, whereby spin-polarized current can flow without a magnetic field.⁵,⁶ It is noteworthy that the electrical and magnetic properties are sensitive to interface structures such as zigzag/armchair edges and carbon–boron/ carbon–nitrogen bonds. To realize and exploit such fascinating functions, it is, therefore, highly desirable to prepare in-plane heterostructures with uniform and structure-controlled interfaces.

The synthesis of such in-plane heterostructures has recently been achieved by chemical vapor deposition (CVD).⁷⁻¹³ Some previous studies have revealed that the edges of first-grown graphene grains can be used as nucleation sites for secondary hBN growth.⁹⁻¹¹ In particular, Liu et al. reported scanning tunneling microscopy (STM) observations indicating that hBN has an atomic smoothly connection to graphene at the interface.¹¹ Furthermore, when hBN was grown from the zigzag edges of graphene, the orientation of the honeycomb lattice of hBN grains was found to be affected by that of the templated graphene grains rather than by the lattice of the underlying Cu surface.¹¹ This indicates that the interface structure could have two possible forms, carbon–boron and carbon–nitrogen bonds, at the zigzag-edge interface, as shown in Fig. 1(a). Even though theoretical studies have predicted that carbon–boron bonds have a higher stability than carbon–nitrogen bonds,¹⁰,¹⁴ the forms that are favorable in actual systems and the crystal orientation of hBN grown epitaxially from graphene edges have yet to be clarified.

In this work, we investigated the crystal orientation of monolayer hBN grains grown epitaxially from the zigzag edges of graphene. Low-energy electron microscopy (LEEM) observations revealed that the crystal orientation of individual hBN grains is dependent on the direction of the templated zigzag edges of graphene. Furthermore, we used the triangular atomic defects in hBN to confirm the orientation of hBN grains through high-resolution transmission electron microscopy (HRTEM) observations. The results indicate that the epitaxially grown hBN orientation is determined by the formation of carbon–boron bonds at the graphene/hBN interface, which provides a promising way of producing uniform interface structures and orientation-controlled hBN grains.

Monolayer graphene and hBN in-plane heterostructures were grown on Cu foil by a two-step CVD process based on a previously reported method.¹⁵ Graphene was grown by the atmospheric-pressure CVD of methane on commercial Cu foils (Nilaco, 99.9%, 20 μm thick). The Cu foil was placed in a quartz tube (3 cm in diameter, 100 cm in length) that was then filled with Ar/H₂ (3%) gas at a flow rate of 400
cm³/min, and annealed at 1,050 °C for 1 h in an electric furnace. Growth was performed at 1,050 °C for 30 min under a gas mixture of Ar/H₂ (3%)/CH₄ (0.0033%) at a flow rate of 150 cm³/min. After the graphene growth, the quartz tube was filled with Ar/H₂ (3%) gas at a flow rate of 200 cm³/min at 1,050 °C for 20–30 min to perform the H₂ etching of graphene. For hBN growth, 5 mg of an ammonia borane (NH₃–BH₃; Aldrich) was sublimated at 70–80 °C using a water bath and then introduced into the reaction region annealed at 1,050 °C through the Ar/H₂ gas flow at 200 cm³/min under atmospheric pressure. After reaction for 15–30 min, the sample was immediately cooled to room temperature.

Scanning electron microscopy (SEM; JEOL JSM-6360F) observations were conducted at a beam energy of 2 kV. A LEEM device (Elmitec LEEM III) was used to obtain bright-field (BF) and dark-field (DF) images, and low-energy electron diffraction (LEED) patterns of the sample. Room-temperature HRTEM (JEOL JEM-2100F) observations and electron energy loss spectroscopy (EELS) were conducted at 80 keV with a current density of approximately 0.1 pA/nm² under a pressure of 10⁻⁶ Pa. For both HRTEM and EELS measurements, the sample was transferred from the Cu foil to a SiN grid with 2-µm-diameter holes by a polymer transfer method.¹⁵

Figures 1(b) and 1(c) show typical SEM images of hexagonal graphene grains without H₂ etching on Cu foil before and after hBN growth. Ribbon-shaped hBN growth from the edge of the graphene grains was observed. The coverage of hBN can be simply controlled by adjusting the growth time. It is noted that the nucleation of hBN occurs mainly from the graphene edge and that the formation of isolated hBN grains is suppressed compared with our previous work.⁹ This is due to the extremely clean and flat surface of the Cu foil and the continuous hBN growth without air exposure after graphene growth.

An increase in the density of graphene/hBN interfaces is favorable for LEEM and HRTEM observations. For this purpose, H₂ etching was used to generate hexagonal holes with zigzag edges in the graphene grains, as reported previously.¹⁶ Figure S1 in the online supplementary data at http://stacks.iop.org/APEX/10/055102/mmedia shows that the graphene grains on Cu foil have many 1–2-µm-diameter hexagonal holes after H₂ etching. It is noted that the edges generated by the present H₂ etching have the same direction as the zigzag edges of pristine graphene grains. The zigzag directions of grain edges obtained under the present conditions have been confirmed by using the rotationally calibrated electron diffraction patterns obtained in our previous study.¹⁷ Figure 2(a) shows that hBN can be grown from the edges, both inside and outside graphene grains, during CVD with the ammonia–borane source gas.

Figures 2(b)–2(d) present the BF and DF LEEM images of the graphene/hBN in-plane heterostructures. The BF image was taken at an electron energy of 2 eV, whereby three hexagonal hBN grains with a relatively dark contrast can be observed [Fig. 2(b)]. To record the DF images at 58 eV, two different diffraction spots were used to distinguish hBN grains with opposite crystal orientations, as reported previously.¹⁸ The diffraction spot of hBN monolayers has threefold symmetry owing to the difference in the sublattices of boron and nitrogen atoms, in contrast to that of graphene.¹⁹ This allows us to separately visualize inverted hBN grains, as shown in Fig. 2(e). The two DF images clearly show that the individual hexagonal hBN grains in the BF image consist of six grains, as schematically illustrated in
Figs. 2(f) and 2(g). It is noted that graphene can be brightly observed in both two DF images because of its sixfold symmetry. Similar consistent results were obtained from the DF-LEEM images of other regions (Fig. S2 in the online supplementary data at http://stacks.iop.org/APEX/10/055102/mmedia). In contrast, in the absence of graphene, two opposite crystal orientations were randomly grown on Cu foil, as observed in hBN growth on a Co surface.18) It is noteworthy that these LEEM results indicate that the crystal orientation of hBN grains is determined by the direction of the zigzag edges of graphene grains, and that the specific bonds of either carbon–boron or carbon–nitrogen were preferably formed at the interface.

To obtain further information of the interface structure and crystal orientation of hBN, the triangular atomic defects in hBN were used to confirm the orientation of hBN grains via HRTEM observations. When hBN is under electron irradiation, boron monovacancies are frequently generated, in which triangular atomic defects, i.e., nitrogen-terminated zigzag edges, are grown by the so-called knock-on effect of the incident electron beam.20) Therefore, these triangular defects can be used to determine the crystal orientation of hBN grown from graphene edges.

Prior to the characterization of the defects, the interface between graphene and hBN was confirmed by TEM observations. Figure 3(a) shows a BF-HRTEM image around the interface of graphene and hBN junction. The contrast of each monolayer is almost the same as that in the BF-HRTEM image for graphene and hBN regions because the atomic mass of these elements is almost the same, and mesh-like surface impurities are evident over the entire region. It is noteworthy that the morphology of adsorbed impurities, such as polymer residues, is different between the graphene and hBN surfaces, probably owing to their different electronic properties. This morphological difference can be confirmed in the contrast-enhanced DF image (Fig. S3 in the online supplementary data at http://stacks.iop.org/APEX/10/055102/mmedia) and can thus be used for the rapid identification of the interface location. It is noted that the impurities on graphene tend to have a bright contrast. By this process, the interface was identified as indicated by the red arrows in Fig. 3(a).

The presence of graphene and hBN was also examined using selected-area electron diffraction (SAED) and EELS. The peaks of boron at around 200 eV, carbon at around 300 eV, and nitrogen at around 410 eV in the EELS spectra in Fig. 3(b) reveal that the upper and lower regions correspond to hBN and graphene, respectively. It is noted that a carbon-derived peak in the hBN region originates from the adsorbed impurities such as polymer residues. Figure S4a shows a SAED pattern for the region around the interface indicated by the white dotted circle in Fig. 3(a); spots with sixfold symmetry are observed, which are typical for conventional graphene and hBN. The enlarged image in Fig. S4a in the online supplementary data at http://stacks.iop.org/APEX/10/055102/mmedia shows that each spot is composed of two spots with different distances from the center. In Fig. S4b in the online supplementary data at http://stacks.iop.org/APEX/10/055102/mmedia, the ratio of these two distances is around 1:0.2, which corresponds well to the ratio of the lattice constants of graphene (2.46 Å) and hBN (2.50 Å), thereby indicating the presence of both graphene and hBN within the white dotted circle in Fig. 3(a).

Figures 4(a)–4(c) show the HRTEM images of the triangular atomic defects in the hBN region around the interface at three different locations. Such atomic defects can be generated and enlarged by electron irradiation during HRTEM observations, as shown in Fig. S5 in the online supplementary data at http://stacks.iop.org/APEX/10/055102/mmedia. In contrast, few atomic defects were observed in graphene under the same conditions because of the higher stability of carbon atoms than of boron atoms against the knock-on effect. Defect generation is also a clear indication of the interface region. In each image, the triangular defects have the same orientation because the individual defects have nitrogen-terminated zigzag edges, as observed for the exfoliated single crystals of hBN.20,21) This preferential formation of triangular defects has been explained theoretically by two mechanisms: knock-on damage22) and the formation energy of defects.23,24) The formation energy of defects depends on a variety of factors, such as charge states, edge structures, and edge termination, as predicted by previous theoretical studies.23–27) It is suggested that the triangular vacancies with nitrogen-terminated zigzag edges can form under nitrogen-rich and electron-rich conditions.23,24) In contrast, the difference in the knock-on damage between boron and nitrogen atoms also explains the formation of triangular defects without any additional mechanisms.22)

Most importantly, the side of each triangular defect nearest to the interface [see white arrows in Figs. 4(a)–4(c)] is always parallel to the direction of the interface [red dotted line in Figs. 4(a)–4(c)]. The schematic illustrations shown in Figs. 4(d)–4(f) correspond to the interfaces shown in Figs. 4(a)–4(c), respectively. To realize this crystal orientation of hBN, the interface structures must have carbon–boron bonds. Considering the smooth connection without defects at graphene and hBN interfaces, as observed by STM,11) the present result indicates that the selective formation of carbon–boron bonds during the initial stage of hBN growth from graphene zigzag edges determines the crystal orientation of hBN (Fig. 5). This selectivity presumably results from the higher stability of carbon–boron bonds than of carbon–nitrogen bonds at the interface, as predicted theoretically.10,14) The weaker carbon–nitrogen bonds are explained by the occupation of antibonding states owing to charge transfer from nitrogen to carbon.10)
using LEEM and HRTEM observations. DF-LEEM images revealed that the direction of the graphene zigzag edges fixes the crystal orientation of hBN. Furthermore, triangular atomic defects were used to determine the orientation on monolayer hBN in HRTEM observations, and also indicate the selective formation of carbon–boron bonds at the interface. These results provide a solid basis for the preparation of atomic layer heterostructures with uniform, structure-controlled in-plane interfaces, which are highly desired in order to understand and use their unique electrical and magnetic properties.

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1) S. Okada, M. Igami, K. Nakada, and A. Oshiyama, Phys. Rev. B 62, 9896 (2000).
2) M. Maruyama and S. Okada, J. Phys. Chem. C 120, 1293 (2016).
3) S. Okada and A. Oshiyama, Phys. Rev. Lett. 87, 146803 (2001).
4) Y. Liu, S. Bhowmick, and B. I. Yakobson, Nano Lett. 11, 3113 (2011).
5) Y. Liu, X. Wu, Y. Zhao, X. C. Zeng, and J. Yang, J. Phys. Chem. C 115, 9442 (2011).
6) S. Dutta, A. K. Manna, and S. K. Pati, Phys. Rev. Lett. 102, 096601 (2009).
7) M. P. Levendordor, C.-J. Kim, L. Brown, P. Y. Huang, R. W. Havener, D. A. Muller, and J. Park, Nature 488, 627 (2012).
8) P. Sutter, R. Cortes, J. Lahiri, and E. Sutter, Nano Lett. 12, 4869 (2012).
9) Y. Miyata, E. Maeda, K. Kamon, R. Kitaura, Y. Sasaki, S. Suziki, and H. Shinohara, Appl. Phys. Express 5, 085102 (2012).
10) G. H. Han, J. A. Rodriguez-Manzo, C.-W. Lee, N. J. Kybert, M. B. Lerner, Z. J. Qi, E. N. Dattoli, A. M. Rappe, M. Drndic, and A. C. Johnson, ACS Nano 7, 10129 (2013).
11) Y. Gao, Y. Zhang, P. Chen, Y. Li, M. Liu, T. Gao, D. Ma, Y. Chen, Z. Cheng, and X. Qiu, Nano Lett. 13, 3439 (2013).
12) Y.-C. Lin, C. Jin, J.-C. Lee, S.-F. Jen, K. Suenaga, and P.-W. Chiu, ACS Nano 5, 2362 (2011).
13) T. Gao, X. Song, H. Du, Y. Nie, Y. Chen, Q. Ji, J. Sun, Y. Yang, Y. Zhang, and Z. Liu, Nat. Commun. 6, 6835 (2015).
14) Y. Gao, Y. Zhang, P. Chen, Y. Li, M. Liu, T. Gao, D. Ma, Y. Chen, Z. Cheng, and X. Qiu, Nano Lett. 13, 3439 (2013).
15) Y.-C. Lin, C. Jin, J. C. Lee, S.-F. Jen, K. Suenaga, and P.-W. Chiu, ACS Nano 8, 2362 (2011).
16) Y. Zhang, Z. Li, P. Kim, L. Zhang, and C. Zhou, ACS Nano 6, 126 (2012).
17) M. Fujihara, R. Inoue, R. Kurita, T. Tanouchi, Y. Motoyui, S. Shim, F. Komori, Y. Maniwa, H. Shinohara, and Y. Miyata, ACS Nano 9, 9027 (2015).
18) C. M. Orofere, S. Suzuki, H. Kageshima, and H. Hibino, Nano Res. 6, 335 (2013).
19) Y. Ogawa, B. Hu, C. M. Orofere, M. Tsuji, K. Ikeda, S. Mizuno, H. Hibino, and H. Ago, J. Phys. Chem. Lett. 3, 219 (2012).
20) C. Jin, F. Lin, K. Suenaga, and S. Iijima, Phys. Rev. Lett. 102, 195505 (2009).
21) N. Alem, R. Erni, C. Kisielowski, M. D. Rossell, W. Gannett, and A. Zettl, Phys. Rev. B 80, 155425 (2009).
22) J. Kotakoski, C. Jin, O. Lehtinen, K. Suenaga, and A. Krasheninnikov, Phys. Rev. B 82, 113404 (2010).
23) S. Okada, Phys. Rev. B 80, 161404 (2009).
24) S. Urusaki and H. Kageshima, Jpn. J. Appl. Phys. 56, 025201 (2017).
25) A. Yamanaka and S. Okada, Sci. Rep. 6, 30653 (2016).
26) R. Mukherjee and S. Bhowmick, J. Chem. Theory Comput. 7, 720 (2011).
27) B. Huang and H. Lee, Phys. Rev. B 86, 245406 (2012).