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Atomic-scale imaging of few-layer black phosphorus and its reconstructed edge

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Black phosphorus (BP) has recently emerged as an alternative two-dimensional semiconductor owing to its fascinating electronic properties such as tunable band gap and high charge carrier mobility. The structural investigation of few-layer black phosphorus, such as identification of layer thickness and atomic-scale edge structure, are of great importance to fully understand its electronic and optical properties. Here we report atomic-scale analysis of few-layered BP performed by aberration corrected transmission electron microscopy (TEM). We establish the layer-number-dependent atomic resolution imaging of few-layer BP via TEM imaging and image simulations. We also find that the electron beam can be utilized to form BP nanoribbons with crystalline edge structures. Atomic resolution imaging of BP clearly shows the reconstructed edge structures, which is also corroborated by van der Waals first principles calculations on the edge stability. Our study on the precise identification of BP thickness and
atomic-resolution imaging of edge structures will lay the groundwork for investigation of few-layer BP, especially BP in nanostructured forms.

A century after its discovery,1-3 black phosphorus (BP) has regained much attention as an alternative two-dimensional (2D) material owing to its promising electrical, optical and chemical properties.4-19 As a layered structure, BP has the largely tunable bandgap as a function of the number of layers (0.35 – 2.0 eV), which can bridge the missing band-gap range from the currently available various 2D materials.9,15,16,20 BP also poses various interesting electrical, mechanical, and optical properties, such as large tunability by strain20-22 and high in-plane anisotropy.11,16,23-25 Moreover, researchers have recently demonstrated the high charge carrier mobility from few-layer BP5,6,8,15,16 opening up various interesting electronic applications5,26,27 and fundamental studies.10,11

Atomic-scale structural analysis of few-layer BP is essential to fully understand its electronics and optical properties. The various defects28,29 have a profound effect on charge carrier dynamics, which becomes more important for the few-layer form of BP. BP nanoribbons also have various interesting properties, including edge-type-dependent electronic properties and special edge states, as shown by recent theoretical studies.22,30-32 Until now, only a few experimental results on the structural characterization of BP using various microscopy techniques have been reported.9,33-35 Although these reports provide general structural analysis on BP, atomic-scale imaging and analysis of structural modification of BP are mainly unexplored at this point.

Here we report atomic-scale analysis of few-layered BP performed by aberration corrected transmission electron microscopy (TEM). We establish the layer-number-dependent atomic resolution imaging of few-layer BP via TEM experiments and image simulations. In addition, we find that the electron beam can be utilized to form BP nanoribbons with crystalline edge structures.
TEM imaging reveals that the BP edge shows the reconstructed edge configuration, which is also confirmed by first principles calculations with van der Waals dispersion force method. Our study on the precise identification of BP thickness and atomic resolution imaging of BP edges will lay the groundwork for investigation of electrical and optical properties of BP nanostructures.

For TEM analysis, few-layer BP samples are prepared using the conventional mechanical exfoliation and transfer method. (See Method for details.) During the sample preparation process, we minimize sample's exposure time to ambient environment in order to reduce sample degradation. Optical characterizations before TEM analysis are not performed on samples because of possible photon-induced degradation. Figure 1a shows a low-magnification TEM image of a typical BP flake. Without tilting samples, BP usually exhibits the crystal direction viewed along zone axis [010] as shown in Fig. 1b and 1d. The Fourier transform of the image clearly shows the diffraction signal with lattice parameters which are consistent with previous results (Fig. 1e and Table S1). The figure 1f shows the enlarged view of the dashed box in Figure 1d, which agree well with the simulated TEM image (Fig. 1g) at reasonable simulation conditions, thickness and defocus value of 21 nm and 6 nm.

Some transferred BP flakes display folded edge structures and this allows us to observe BP at different crystallographic directions, even without tilting of samples. Figure 1h shows a TEM image around the flake edge where the crystal structure at zone axis [100] is clearly observed. At [100] zone axis, the puckered layered structure of BP can be clearly observed. The interlayer distance of BP is found to be 5.27 Å, which is consistent with previously reported results. The zoom-in image and simulated image are also in a good agreement with simulation conditions of thickness of 20 nm and defocus value of 7 nm. With tilting of the specimens, atomic resolution imaging at extra zone axes is also performed as shown in Supplementary Figure S1. Especially, atomic resolution TEM images from [101] zone axis can differentiate AB and AA stacking and our observation indicate that bulk BP
has mainly AB stacking (Supplementary Figure S1f-j). Our energy calculations for different stacking also confirm that AB stacking is the most stable stacking configuration (Supplementary Figure S2). We also find that all the lattice parameters and d-spacing values are consistent with previously reported values, which is summarized in Table S1.

The precise and facile identification of BP thickness is a prerequisite for investigation of various properties. Figure 2 summarizes how the number of BP layers can be identified through atomic resolution TEM imaging and simulations. Figure 2a shows the TEM image of much thinner (three to seven layers) BP specimen where the thickness is not homogeneous in the different locations due to electron-beam-induced sputtering (Supplementary Figure S3). The comparison of the intensity modulation and its pattern along c-axis of BP is performed between observed TEM images and simulation results. Since the phase contrast TEM image depends on the number of BP layers and defocus value, we perform a series of image simulations along [010] zone axis as a function of the layer number as well as the defocus value, where we assume the AB stacking (Supplementary Figure S4). One thing to note is that even and odd layer numbers produce distinct image patterns. Simulations with even number of layers (for example, double layer) show the intensity modulation with the half of usual bulk lattice parameters due to the symmetric AB stacking. On the other hand, with an odd number of layers (monolayer and triple layer), the simulated images display the intensity modulation with the periodicity of usual lattice parameters of bulk BP.

We assign the layer numbers and defocus values for the observed TEM images by comparison with simulated images. For example, top image of Figure 2b, the zoom-in image of marked regions A in Figure 2a, shows the distinct image pattern which can originate from the negative defocus values around -6nm and odd number of layer. To assign the precise layer number, we compare the intensity line profiles along the crystal c-axis between the simulated and observed TEM images (Figure 2c). The experimentally observed and simulated TEM image intensity
modulation differ by a factor of two, which is often called the Stobb’s factor.\textsuperscript{36-38} After taking account of this factor, the simulation intensity pattern with 5 layers matches the observation. The TEM images obtained from other locations of the specimen also undergo a similar process and we assign the number of layers and defocus values (Figure 2d), which is also confirmed by the intensity modulation analysis (Supplementary Figure S5 and Table S2) along c-axis (Figure 2e). We find that the BP specimen imaged in Figure 2a has a thickness ranging from three to seven layers.

Now we start our discussion on the edge structure of BP. The investigation of edge structure of BP is an important topic as it significantly influences various physical properties of BP. There are a few recent studies on BP edges and nanoribbons, especially by theoretical calculations.\textsuperscript{30,31} However, there is still a limited number of experimental studies on BP edges.\textsuperscript{33} As shown in Supplementary Figure S4, as-prepared BP specimens exhibit amorphous edge structure, where the amorphous edge regions of several nanometers are always observed. This amorphous edge is possibly due to the degradation during the sample preparation process.

The edge structure of BP crystals can be structurally modified by e-beam irradiation during TEM imaging.\textsuperscript{39} Remarkably, the crystalline edge structure can be obtained via this method. Figure 3a and 3b shows the changes of sample over 15-second e-beam exposure. The atoms at the amorphous edge (indicated by yellow arrows in Figure 3a) can be preferentially sputtered out, exposing the crystalline edge structure. The crystal direction of exposed edge shows zigzag (ZZ) edge direction. Figure 3c is the zoom-in image of BP edge where the periodic edge structure over five unit-cells is clearly observed. Moreover, the image pattern at the edge shows a higher intensity modulation compared to the basal plane. This strongly suggests that there is the reconstructed edge formation.

To have a better understanding on atomic-scale structure of ZZ edge, we calculate the relaxed edge structures with various possibilities using first principles calculations with van der Waals
interactions (See Methods). We find that reconstructed ZZ edges (type 1 and type 2) exhibit similar edge formation energies compared to zigzag (ZZ) or armchair (AC) edge configurations (Supplementary Figure S6). To compare with experimental TEM images, a series of image simulations assuming different ZZ edge structures including usual ZZ edge termination (Supplementary Figure S8) and two types of reconstructed edge configurations are undertaken (Supplementary Figure S9 and S10). Since the observed area has three-layer thickness, which is determined by the previous image pattern and intensity modulation analysis, we focus on the simulated images from triple-layer. By comparison, we find that the observed ZZ edge is consistent with the type-2 ZZ edge reconstruction (Figure 3d). The usual ZZ edge without reconstruction (Figure 3g and 3h) and the type-1 reconstructed edge (figure 3i and 3j) are not consistent with the observed image. We note that the observed type-2 reconstructed ZZ edge was theoretically studied together with some experimental evidence but the direct atomic resolution edge imaging was not previously performed.33

Finally, we discuss the sample thinning and BP nanoribbon formation induced by electron beam irradiation. Figures 4a-e show a time series of structural modification of BP under electron beam. The same series of images are overlaid with different colors in Figures 4f-j for easy identification of structural changes. Different colors indicates triple-layer region (blue), thicker area (pink) and amorphous regions (yellow). The sample thinning with electron-beam sputtering is observed from Figure 4f and 4g; the region overlaid with pink color (thicker area) is gradually replaced by the blue region (three layers).

Electron-beam is one of useful ways to manipulate the materials at nanoscale and we demonstrate that BP nanoribbons can be formed by prolonged e-beam exposure. Figure 4d and 4i clearly show that the formation of approximately 4nm-wide BP nanoribbons with crystalline edge. After prolonged e-beam irradiation, the BP nanoribbon is amorphized to form amorphous BP nano-
constriction with a less than 2 nm neck width. Consequently, the nano-constriction breaks down (See Supporting Movie). The sputtering mechanisms during TEM imaging including calculations of knock-on damage threshold for phosphorene will be an important experimental issue and we are currently investigating this effect in detail.

In conclusion, the atomic-scale structure of few-layered BP and its reconstructed ZZ edges were investigated by Cs-corrected TEM and imaging simulation. The precise and facile characterization methods of BP thickness demonstrated in our study will lead to various fundamental studies, such as measurements of layer-number-dependent electrical and optical properties. We also demonstrate that electron beam irradiation can be used to form BP nanoribbons as well as to expose crystalline reconstructed ZZ edge. Further TEM analysis on BP is expected to shed light on various defect structures and structural degradation mechanisms.
Methods

**Black phosphorus sample preparation:** Black phosphorus (BP) crystals were purchased from Smart Elements (purity, ~99.998%). To prepare TEM samples, BP flakes were exfoliated onto SiO2/Si wafers using conventional mechanical exfoliation method. Exfoliated BP flakes were transferred to Quantifoil Au TEM grids using direct transfer method.40 To thin BP flakes and remove surface residues, gentle plasma cleaning with H2 and O2 gas environment was carried out using plasma cleaner (Advanced plasma system, Gatan, USA) for 5 minutes with 10 W input power. To minimize the oxidation of BP specimens, BP samples were immediately loaded into TEM chamber after sample preparation process.

**TEM characterizations and image simulations:** The atomic resolution imaging of BP were performed with a FEI Titan G2 operated at 80 kV, which is equipped with image Cs aberration corrector and monochromator. For the TEM time series, the exposure time of 0.3 seconds together with the processing time of 0.25 seconds were used. This results in the image frame time of 0.55 second per image. All the TEM image simulations were performed using MacTempas software. The BP crystal structure of BP with a=3.31 Å, b=10.48 Å and c=4.37Å (space group Cmca41) were used. The b-axis is the layer stacking direction.

**Theoretical calculations:** Calculations were based on *ab initio* density functional theory using the SIESTA method42 and the VASP code43,44. The generalized gradient approximation45 along with the optB88-vdW46,47 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. Projected augmented wave method (PAW)48,49 for the latter, and norm-conserving (NC) Troullier–Martins pseudopotentials50 for the former, have been used in the description of the bonding environment for P. NC pseudopotentials include non-linear-core corrections (NLCC)51 to correctly account for the weak interactions between core and valence densities. The pseudocore radii $r_{NLCC}(a_o)$ (in Bohrs) together with the different l channels $r_l(a_o)$ have been optimized and the values are: $r_s(a_o)$=1.83, $r_p(a_o)$=1.83, $r_d(a_o)$=1.83, $r_f(a_o)$=1.83, $r_{NLCC}(a_o)$=1.45. The shape of the NAOs was automatically determined by the algorithms described in42. The cutoff radii of the different orbitals were obtained using an energy shift of 50 meV, which proved to be sufficiently accurate to describe the geometries and the energetics. Atomic coordinates were allowed to relax until the forces on the ions were less than 0.04 eV/Å under the conjugate gradient algorithm. Further relaxations (0.01 eV/ Å) do not change appreciably the energetics and geometries. The lattice constants for the monolayer unit cell were optimized and found to be $a$=3.297 Å, $b$=22.1220 Å, $c$=4.655 Å in Siesta which is in good agreement with the
results obtained using Vasp, a=3.295 Å, b=22.1219 Å, c=4.535 Å. To model the system studied in the experiments, we created large supercells containing up to 136 atoms to simulate the interface between different nanoribbon layers and edge reconstructions in the phosphorene. To avoid any interactions between supercells in the non-periodic direction, a 20 Å vacuum space was used in all calculations. In addition to this, a cutoff energy of 100 Ry was used to resolve the real-space grid used to calculate the Hartree and exchange-correlation contribution to the total energy. For the phosphorene sheets, the Brillouin zone was sampled with a 10x8x1 grid under the Monkhorst-Pack scheme, which gives similar results as those using a finer 17x15x1 k-sampling. In addition to this we used a Fermi-Dirac distribution with an electronic temperature of $k_B T = 20 \text{ meV}$.

**Acknowledgements**

This work is supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2014R1A1A2058178). D.S. thanks the studentship from the EPSRC-DTP award. E.J.G.S. acknowledges the use of computational resources provided by the Atomistic Simulation Center, and the Extreme Science and Engineering Discovery Environment (XSEDE), supported by NSF grants number TG-DMR120049, TG-DMR150017; as well as the Queen’s Fellow award through the startup grant number M8407MPH.
Figure 1. TEM analysis of black phosphorus (BP) at various crystal zone axes. (a) Low magnification TEM image of a BP sample. Scale bar, 500nm. (b,c) Atomic model of BP shown at [010] and [100] zone axes, respectively. (d) TEM image of the BP at [010] zone axis. Dashed box is the field of view for panel f. Scale bar, 2nm. (e) Fourier transform of panel d. The circles indicate low-index diffraction spots. (f) Enlarged view of the dashed box in panel d. Scale bar, 0.5nm. (g) TEM image simulation result from the crystal structure shown in panel b. The locations of phosphorus atoms are overlaid as circles. (h) TEM image of a BP flake at [100] zone axis. Scale bar, 2nm. (i) Fourier transform of panel h. The circles indicate low-index diffraction spots. (j) Enlarged view of box in panel h. Scale bar 0.5nm. (k) Simulated TEM image from the crystal structure shown in panel c.
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Figure 3. Atomic resolution TEM images of BP edges. (a) TEM image of amorphous structure at BP edge sites as indicated by yellow arrows. Scale bar, 1nm. (b) Crystalline BP edge produced by e-beam irradiation. The image was acquired after 15 sec e-beam irradiation from panel a. Atoms at amorphous edge are etched by e-beam and consequently crystalline edge is exposed. The red box is the field of view for panel c. Scale bar, 1nm. (c) Zoom-in image of the BP edge. Scale bar, 0.2nm. (d) Atomic model of type-2 reconstructed ZZ edge configuration in triple-layer BP. The atomic layer at the bottom (red) is overlapped with the top layer (blue). (e) TEM image simulation of the atomic model in panel c. Defocus value is -2nm. (f) The same simulation image with atomic model overlay. (g) Atomic model of regular ZZ edge configuration without reconstruction. (h) TEM image simulation of regular ZZ edge structure. Defocus value is -2nm. (i) Atomic model of type-1 reconstructed ZZ configuration of triple layer BP. (j) TEM image simulation of the atomic model in panel i. Defocus value is -2nm.
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Reference


Supporting Information for

Atomic-scale imaging of few-layer black phosphorus and its reconstructed edge

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Table S1. Comparison of BP various d-spacing with previous literatures. (Unit: Å)

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Supplementary Movie 1. A time series of TEM images of phosphorene nanoribbon formation.
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