Fabrication of a Freestanding Boron Nitride Single Layer and Its Defect Assignments

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A freestanding single layer of hexagonal boron nitride (*h*-BN) has been successfully fabricated by controlled energetic electron irradiation through a layer-by-layer sputtering process. We have successfully resolved atomic defects in *h*-BN with triangle shapes by means of an aberration corrected high-resolution transmission electron microscopy with exit-wave reconstruction. Boron monovacancies are found to be preferably formed and the dominating zigzag-type edges are proved to be nitrogen terminated.

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Low dimensional materials such as graphene and carbon nanotubes continue to gather wide interest from physical scientists [1]. Hexagonal boron nitride (*h*-BN) has a similar two-dimensional structure with a distinct chemical species and exhibits completely different physical properties from graphene [2,3]. Even though it is quite important to compare the defect structures of *h*-BN (threefold symmetry) with graphene (sixfold symmetry), very little is known about the atomic defects of *h*-BN. In order to clarify the lattice defects in *h*-BN such as vacancies or edges, the individual boron and nitrogen atoms should be directly imaged and even distinguished; otherwise the precise defect structures cannot be deduced.

High-resolution transmission electron microscopy (HRTEM) successfully identified single carbon atoms ($Z = 6$) [4,5]; nevertheless, single atoms with a smaller atomic number have never been successfully imaged with the elemental assignment. A crystal structure $LiCoO_2$ has been recently atomically resolved, but the Li atoms ($Z = 3$) are imaged only in atomic columns, not as single atoms [6]. We have employed an aberration corrected HRTEM and the exit-wave (EW) reconstruction [7] to discriminate the boron and nitrogen atoms within a single layer *h*-BN. The EW reconstruction method involving a series of through focus HRTEM images is beneficial to discriminate the boron and nitrogen atoms, since we could enhance the high-spatial-frequency components and retrieve the phase image.

The *h*-BN specimens with a reduced number of layers were first prepared, and then were further thinned locally down to single layers *in situ* by electron beam irradiation at 120 kV inside the TEM. The single layer of *h*-BN can be thus prepared within a desired region in a well-controlled manner (see Ref. [8] for the sample preparation process in detail). During the electron beam thinning process, many lattice defects such as vacancies have been inevitably induced. Figure 1(a) shows a HRTEM image of typical defect structures found on a *h*-BN monolayer. The HRTEM image was recorded with a fixed defocus value after a prolonged irradiation (about 240 sec later). One can see the triangle-shaped holes (or vacancies) with various sizes, which have been created mainly due to the knockon effect of the incident electron beam. From the present image we are unable to deduce the exact atomic structure of these defects because the boron and nitrogen atoms cannot be distinguished. But one can notice the following important points: (i) the triangle-shaped holes have discrete sizes, (ii) the smallest triangle is located at the corner

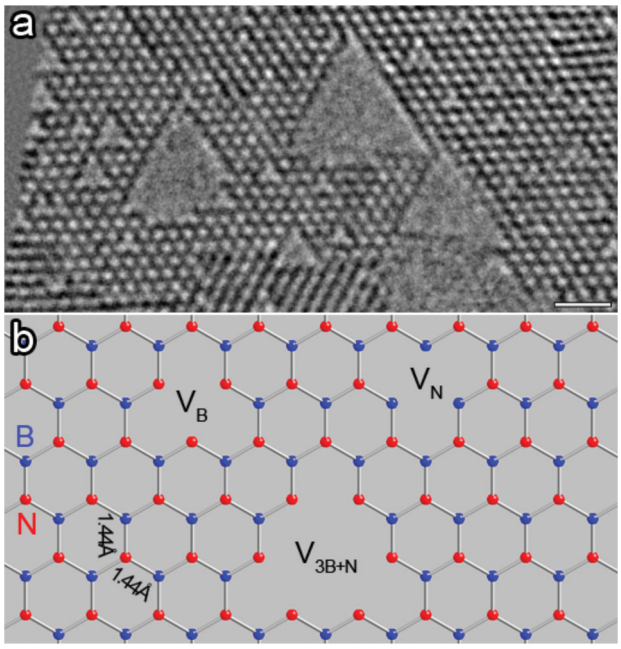

FIG. 1 (color). Atomic defects in *h*-BN monolayer. (a) A typical HRTEM single frame showing the lattice defects in *h*-BN such as monovacancies (one lattice atom missing) and even larger vacancies, all of which are triangle shape with the same orientation. (b) Models for the atomic defects in *h*-BN. V_B and V_N stand for boron and nitrogen monovacancy, respectively. Note that the V_B and V_N should have an opposite orientation, while the V_B and V_{3B+N} (missing three boron and one nitrogen atoms) are in the same orientation and surrounded by two-coordinated nitrogen atoms. Scale bar = 1 nm.

of three bright spots (hexagons) and should correspond to the monovacancy, (iii) all of the defects have a nearly normal triangle shape, and (iv) all the triangles are exactly in the same orientation.

Let us consider the models for monovacancy and multivacancy in h-BN single layer [Fig. 1(b)]. Monovacancy of boron (marked as V_B) consists of one missing boron atom. Three neighboring atoms are the doubly coordinated nitrogen. Nitrogen monovacancy (V_N) shows an opposite atomic configuration for boron atoms. V_{3B+N} is a multivacancy where three boron and one nitrogen atoms are missing and is surrounded by six (doubly coordinated) nitrogen atoms. From the experimental fact that all the triangles are in the same orientation, one can conclude that the V_B and V_N will not coexist because two types of vacancies should give rise to different orientations [Fig. 1(b)]. (Note that $V_B, V_{3B+N}, V_{6B+3N}, \ldots$ have the same orientation, and $V_N, V_{B+3N}, \ldots$ should have the opposite.) Therefore it is quite essential to distinguish the monovacancy site of the BN layers to corroborate the dominant defect structures.

We first try to distinguish the individual boron and nitrogen atoms in a perfect hexagonal lattice of BN monolayer by means of EW reconstruction. The phase image after reconstruction [Fig. 2(a)] clearly shows the hexagonal network of the bright spots, which indeed correspond to the individual atoms in the h-BN network. (Note that the monolayer region is in the middle and the bilayer can be also seen at the top and bottom of the image.) As easily noticed in an amplified image [Fig. 2(b)], the atoms within the hexagonal network exhibit two different brightnesses to reflect the contrast difference for the individual boron and nitrogen atoms. The heavier nitrogen atoms should appear in brighter contrast. From the line profile of the contrast in their phase image in Fig. 2(c), the relative phase shift ratio of B/N is measured as about 0.8. The measured B-N bond length is about 1.44 ± 0.1 Å for the nondefective region, corresponding to an in-plane lattice constant of about 2.49 Å, matched well with the theoretical prediction [9], which is also very close to that of bulk h-BN (2.50 Å).

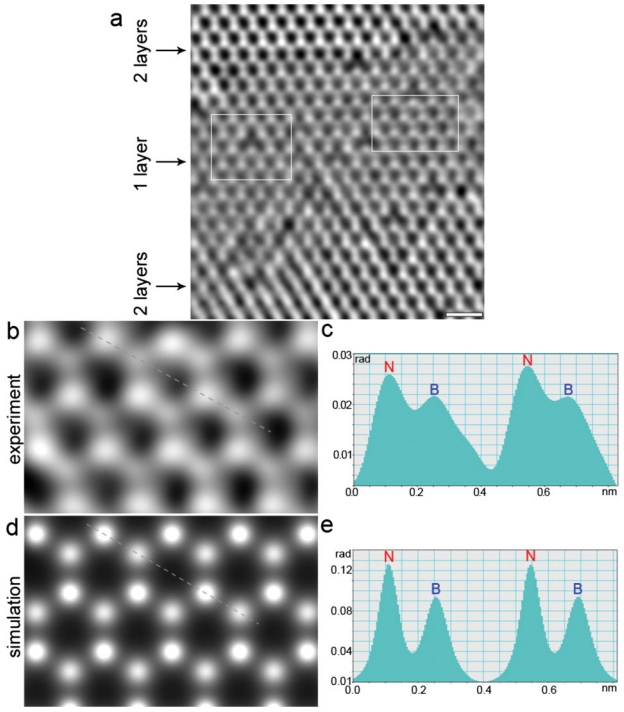

FIG. 2 (color). Elemental discrimination of lattice atoms in h-BN monolayer. (a) The phase image of reconstructed exit wave of the same region. (b) A zoomed image of the marked area in (a) where the individual boron and nitrogen atoms are clearly discriminated. (c) A line profile from the trace in (a). (d) Simulated phase image of h-BN monolayer. (e) A line profile from the trace in (d). Scale bar = 0.5 nm.

We have performed an image simulation (using MACTEMPAS) on the h-BN monolayer. Despite the apparent difference in spatial resolution, our experimental results of the phase [Fig. 2(b)] can overlap precisely with the simulated phase [Fig. 2(d)]. Note that the simulated phase image is perfectly ideal and its resolution is naturally higher than the reconstructed phase. The line profile [Fig. 2(e)] is traced as labeled in Fig. 2(d), which shows a qualitative match with the experimental line profile, in terms of the distance between boron and nitrogen atoms and the phase shift ratio (~0.8). The agreement between the experimental and simulated line profiles clearly proves that both are directly imaged and distinguishable. The magnitude of the simulated phase shifts is about 5 times higher than the experimental one, despite the fact that the absolute specimen thickness is known. Such a discrepancy between the experimental and simulated data on their magnitudes was also mentioned in other reports [5,10] and can be related with the so-called "Stobbs factor" [11]. Even though the above result is sufficient to discriminate the monovacancy sites because the local polarity has already been revealed, we further continue to get the direct image of vacancies.

Figure 3(a) shows a reconstructed phase image of a vacancy region. One can directly see that an atom less bright is missing from the hexagonal network. It can be therefore assigned as a boron monovacancy (V_B) and can also be confirmed from the line profile in Fig. 3(b). All the monovacancies we have examined are the V_B and no nitrogen monovacancies (V_N) are found. The $V_{3B+N}, V_{6B+3N}, \ldots$ (the triangles in the same orientation as V_B) are also identified for the multivacancies, but not the $V_N, V_{B+3N}, \ldots$. This fact indicates that the boron can be more easily removed and all the edge-terminating atoms around the vacancies should be doubly coordinated nitrogen atoms.

The local structure around a missing boron atom is found to be substantially deformed: the measured distances between the pairs of nitrogen atoms surrounding a V_B become 2.63 ± 0.10, 2.71 ± 0.10, and 2.72 ± 0.10 Å, which are slightly larger than that in a perfect h-BN network (about 2.49 Å). Such a slight local reconstruction is

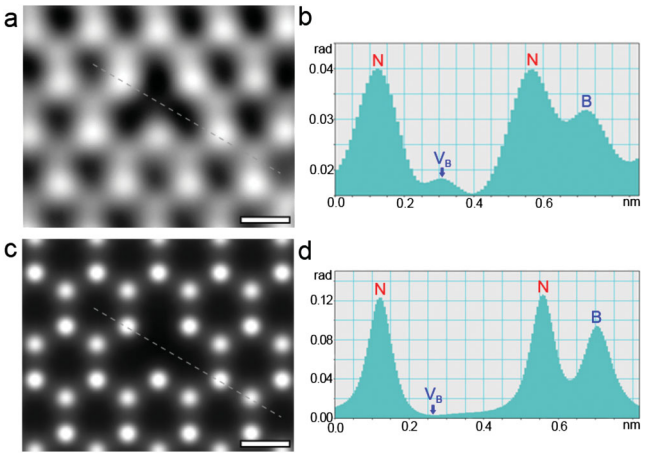

FIG. 3 (color). A boron monovacancy. (a) The phase image of reconstructed exit wave of a region containing a boron monovacancy. (b) A line profile confirms the missing atom is boron. (c) Simulated phase image and (d) line profile involving the boron monovacancy. Scale bar = 0.2 nm.

also consistent with the theoretical studies [9]. Although the out-of-plane distortion has not been considered here in a projected TEM image, such a relaxation should be of importance for the structural stabilization of the V_B. Chemical bonding should be difficult to form between two nitrogen atoms with such a large interatom distance. One dangling bond for each N atom might interact repulsively. This should prevent a pentagon from forming in *h*-BN.

It is also of particular importance to determine the edge structure of the *h*-BN, which was predicted to play an important role on the electronic and magnetic properties in *h*-BN [12–14]. We concentrate on an edge of one of the larger triangle holes, which is in principle equivalent to the open edge. Figure 4(a) shows a HRTEM image taken at a slight underfocus to enhance the contrast of edges. All the edges are zigzag type and appear very neat and sharp. The reconstructed phase image is also shown in Fig. 4(b). Although the quality of phase reconstruction is not as good as that in Figs. 2 and 3 due to the possible instability of open edges, the individual boron and nitrogen atoms were distinguished and marked as blue and red dots, respectively [see Fig. 4(c) for a schematic representation]. The open edge is terminated with the doubly coordinated nitrogen atoms on the outmost atomic chain.

The dominant V_B and no V_N found for monovacancies may be partly correlated with the irradiation induced damage process. Here a fast electron beam with energy of 120 keV was employed for the sample preparation and for the image recording as well. The main damage mechanism should be the knockon, a quasielastic collision between the incident electron and the nuclei of the atoms belonging to the specimen. It is known that boron has a smaller threshold beam energy (about 74 keV) for knockon than that of nitrogen (about 84 keV) [15]; therefore, it is reasonable that the knockon can be more prominent for the boron atoms out of the lattice to form the V_B. Since the energy carried by the incident electrons (120 keV) is larger than the threshold beam energies for knockon of both atoms, the difference of the threshold energy cannot be the only reason for the dominant boron vacancies [16].

The previous theoretical studies (and experimental investigations) claimed that the formation energy of a V_B is larger than that of V_N and that therefore the formation of nitrogen monovacancy should be preferable [17]. These theoretical suggestions may contradict our experimental results. It should be noted that most of these simulations were done based on the thermodynamic equilibrium conditions, which are different from the present experimental conditions. Here the vacancies were created mostly by the high energy charged electrons, and the defect structures cannot be exactly the same as the thermodynamically expected ones.

No topological defect such as five- or seven-membered rings has ever been found throughout our experiments. Even though some theoretical simulations [18,19] have predicted the Stone-Wales transformation [20] in *h*-BN layers, any bond flip or local reconstruction around the missing boron atoms leading to the pentagon should require a large activation energy and is unlikely to happen; similar results were also found in BN nanotubes [21]. This is a good contrast to the case of carbon in which topologi-

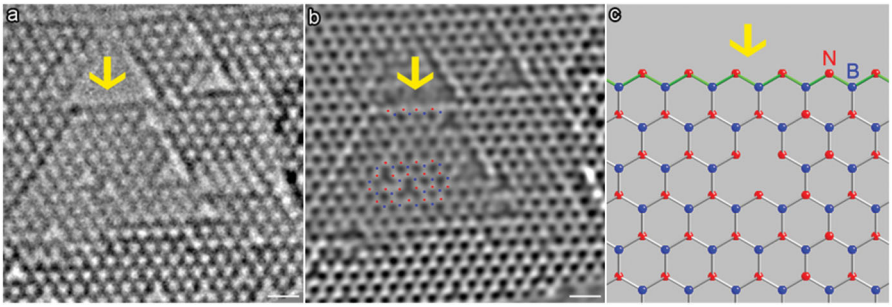

FIG. 4 (color). Nitrogen terminated zigzag edge of a *h*-BN monolayer. (a) A HRTEM single frame of a zigzag edge (indicated by yellow arrow). (b) The phase image of reconstructed exit wave showing the edge is terminated with the nitrogen atoms. (c) A model for the edge structure involving two-coordinated nitrogen atoms. Scale bar = 0.5 nm.

cal defects are preferably formed [4,5,22]. Neither the N-N bond nor B-B bonds are energetically preferable compared to the B-N bond. Obviously, more careful examinations emphasizing the difference between the polarized B-N bond and the nonpolarized C-C bond are needed.

We should also emphasize that no stable divacancy (V_{BN}) has been found in our study, although one of the previous studies pointed out a possibility of a paired vacancy formation under the electron beam irradiation by considering the charge compensation of boron and nitrogen [23]. One can infer that the V_{BN} should immediately transform to the V_{3B+N} due to the further removal of doubly coordinated boron atoms.

In this Letter, we report a novel method to fabricate a single layer of *h*-BN through the controlled energetic electron irradiation induced layer-by-layer sputtering. More importantly, by means of the EW reconstruction of the through-focus image series, individual boron and nitrogen atoms have been experimentally distinguished for the first time. Defects in boron nitride monolayer created by irradiation damage, such as the dominated boron monovacancies and the large vacancies with nitrogen atom terminated zigzag edge, are also atomically resolved. The observed ''unexpected'' defect structures would require more and deeper theoretical inputs. Combining the present experiments with variable energetic irradiation and beam intensity might allow fabricating functional devices with the well-controlled defect structures of the boron nitride semiconductors.

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