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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Figure 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. \( V_\text{B} \) and \( V_\text{N} \) stand for boron and nitrogen monovacancy, respectively. Note that the \( V_\text{B} \) and \( V_\text{N} \) should have an opposite orientation, while the \( V_\text{B} \) and \( V_{3\text{B}+\text{N}} \) (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 $1.44 \pm 0.1$ 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).

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 ($\sim 0.8$). 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 $2.63 \pm 0.10, 2.71 \pm 0.10,$ and $2.72 \pm 0.10$ Å, which are slightly larger than that in a perfect $h$-BN network (about 2.49 Å). Such a slight local reconstruction is
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 repul-
sively. 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, re-
spectively [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 dam-
age 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 mecha-
nism should be the knockon, a quasielastic collision be-
tween 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 in-
vestigations) 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 con-
ditions, 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 re-
quire 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). A boron monovacancy. (a) The phase image of
reconstructed exit wave of a region containing a boron mono-
vacancy. (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.
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 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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[16] It should be noted that a research group claimed that they could prepare the boron monovacancy dominated defect structures by choosing a suitable acceleration voltage of 80 kV, higher than the knockon threshold of boron while lower than that of nitrogen. Despite their speculation, a defective structure with enriched boron monovacancies was still obtained even when a 120 kV acceleration voltage was employed, higher than the knockon threshold for both boron and nitrogen. Therefore, the underlying mechanism required further investigations, not simply depending on the knockon threshold. J. C. Meyer et al., in Proceedings of the 14th European Microscopy Congress, Aachen, Germany, 2008 (Springer, Aachen, 2008).