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Vacancy growth and migration dynamics in atomically thin hexagonal boron nitride under electron beam irradiation

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Atomically thin hexagonal boron nitride (h-BN) is investigated using aberration-corrected ultra-high resolution electron microscopy under 80 kV electron beam. This study focuses on the *in situ* formation, growth and migration of vacancies in h-BN. This study also reveals interaction dynamics of edges and vacancies with adatoms and molecules under the electron beam. According to this investigation, boron monovacancies migrate through their second neighbor to reduce the surface energy of the membrane.

1 Introduction Hexagonal boron nitride (h-BN) is a promising material with a variety of applications in electronics and hydrogen storage [1, 2]. Understanding the mechanisms behind formation and migration of defects in this crystal is essential, since the configuration of defects can have a drastic impact on the resulting physical, chemical and electronic properties of the crystal. Successful isolation of atomically thin hexagonal boron nitride membrane [3, 4] has brought up the possibility of studying the stability and interaction dynamics of defects and edges with adatoms and molecules. In this study we investigate such interaction dynamics in h-BN at low dimensions using aberration-corrected ultra-high resolution transmission electron microscopy.

2 Experiments

2.1 Transmission electron microscopy imaging and analysis Exfoliated h-BN on TEM grid is prepared according to the previously reported procedure [3]. For this investigation, we use the TEAM microscope with the imaging condition optimized to obtain white atom contrast (see Supplementary Information at www.pss-rapid.com). To understand the dynamics of vacancy formation and growth in h-BN, image series were recorded while the membrane was exposed to the electron beam. The movies shown in the Supplementary Information in this study are put together from consecutive images of h-BN taken with the time interval of about 1.5 s.

3 Results and analysis Movie 1 provided in the Supplementary Information shows the interaction of a one- to four-layer h-BN membrane with the electron beam. The 80 keV electron beam causes the membrane to fold after prolonged beam exposure (see Fig. S1 in Supplementary Information). Formation and growth of holes from single mono-vacancies can be observed in this region of the membrane. These dynamics are fast and result from the low knock-on energy threshold of boron at 80 kV [5]. Thus the few-layer h-BN membrane can be exfoliated down to a monolayer [3, 4].

Figure 1 presents selected frames from Movie 2; a magnified region of the h-BN membrane, previously shown in the lower left section of Movie 1. In-situ formation and growth of mono-vacancies and their interaction dynamics with adatoms and molecules can be observed in this region of the film. Figure 1 presents selected snapshots from these dynamics. Figure 1a–c show formation of a single vacancy and its growth into a larger vacancy with a nitrogen-terminating zigzag edge. This vacancy further grows in size (Fig. 1d) after ejection of three more atoms at the edge. Figure 1e shows annihilation of the new vacant sites with three atoms several seconds later. This growing defect is close to the edge of the h-BN sheet with many dynamic edge-atoms constantly repositioning themselves. The white arrows in Fig. 1d and e show formation of a step after a few edge-atoms leave their site at the edge of the film. It is not possible to unambiguously identify the origin of the atoms that filled the empty sites in the vacancy. The departed edge-atoms, however, are considered strong candidates annihilating these vacant sites.

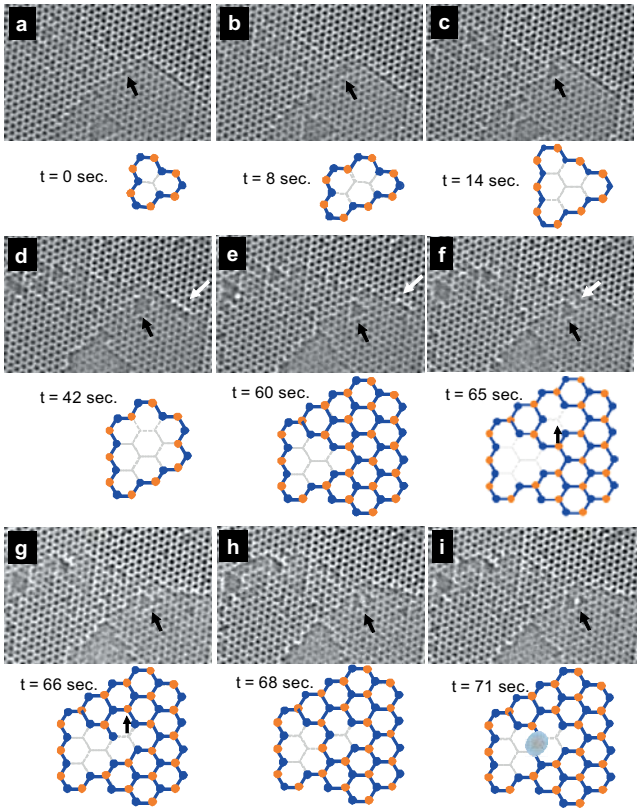

Figure 1 (online colour at: www.pss-rapid.com) h-BN irradiation under the electron beam showing formation of a single monovacancy (a) and its growth into a large triangular vacancy (b and c). Ejection of three more atoms at the vacancy edge leads to a new configuration (d). The new vacant sites are annihilated with adatoms (e). A boron monovacancy (f) is formed (shown by white arrow). A new vacancy arrangement (g) is observed after the new monovacancy is annihilated by a boron atom. The arrow on the atomic models "f" and "g" show diffusion path of the boron atom into the vacancy. Annihilation of the boron vacant site (h) is observed at the border of the two vacancies. (i) A molecule is further trapped on top of the zigzag bridge between the two vacancies. Nitrogen is blue, boron is orange.

Figure 1f shows formation of a boron monovacancy near the large vacancy. This monovacancy moves closer to the large vacancy after a boron atom at the perimeter of the large vacancy migrates into this vacant site (Fig. 1f–g). This migration takes place through a second neighbor in the h-BN lattice, since formation of homo-nuclear bonds, i.e. B–B and N–N, are not energetically favorable in h-BN. Figure 1g shows the vacancy configuration after this migration is complete. A single-bonded nitrogen atom is observed to remain in the lattice at the edge of the vacancy in Fig. 1g. This stability is believed to result from the relaxation of this atom and formation of an interlayer B–N bond at this atomic site [6]. An adatom further annihilates the boron vacant site at the boundary of the two defects (Fig. 1h). A molecule is then trapped at the zigzag bridge between the two neighboring vacancies (Fig. 1i). This adsorption likely occurs due to the presence of dangling bonds at the under-coordinated atoms at the zigzag bridge between the two vacancies. This defect shows more dynamics in the next several seconds. These dynamics are however hard to trace since the diffusion rate of the atoms at this defect site is much faster than our camera recording rate.

Figure 2 shows another example for the interaction of h-BN lattice with the electron beam. These images are selected from Movie 3 in the Supplementary Information. A monolayer of h-BN can be observed at the top left corner of this region. A few mono-vacancies and large holes can be observed with the same orientation in the monolayer area of h-BN, strongly suggesting preferred knock-on damage of boron atoms. The circles indicate the initial (Fig. 2a) and final (Fig. 2d) configurations for the vacancies. The black arrows on the images point to a reference monovacancy that has remained intact during these dynamics. The atomic models in Fig. 2a and d suggest migration of the left monovacancy to the right followed by its growth. This migration path is marked by an arrow on the atomic model in Fig. 2a and b. The two monovacancies coalesce through diffusion of the second neighbor boron atom into the left monovacancy. After this diffusion, an unstable transition state is reached with a single-bonded nitrogen atom at the edge of the vacancy (Fig. 2b). The nitrogen atom is ejected from the membrane due to its low knock-on energy thresh-

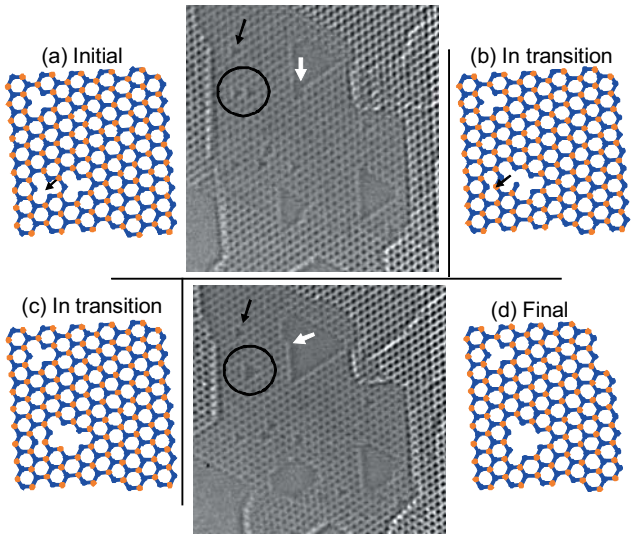

Figure 2 (online colour at: www.pss-rapid.com) TEM images showing formation and migration of boron monovacancies in a monolayer of h-BN. Two neighboring monovacancies (a) are in the circle with respect to the reference monovacancy, pointed by a black arrow. Two transition states (b and c) after the boron atom at the perimeter of the monovacancy fills up the monovacancy on the left side. (d) Formation of a stable triangle vacancy with nitrogen terminating zigzag edges after vacancy migration. The white arrows on the images show the steps at the membrane edge under the electron beam. Nitrogen is blue, boron is orange.

old leaving a double-bonded boron atom (Fig. 2c) [5]. Boron at the edge is ejected due to its low displacement threshold [5], leading to the formation of a large stable triangle vacancy with nitrogen terminating zigzag edges (Fig. 2d). In this study we do not observe migration of isolated monovacancies. In contrast, neighboring monovacancies are often observed to migrate towards each other and coalesce forming a larger vacancy. The driving force behind this migration is to reduce the surface energy of the membrane [7].

Figure 2 also indicates the dynamics of the edges at the holes in the h-BN membrane as the atoms are sputtered away. The white arrows on the images in Fig. 2 point to a hole with zigzag edge configuration. Careful observation of this movie shows that the individual edge-atoms are ejected from the membrane consecutively. Unlike graphene [8], these dynamics seem to occur in a structured order, where ejection of one atom leads to the ejection of its first nearest neighbor along the zigzag edge. The atomic model in Fig. 2d depicts the zigzag edge structure with a step next to the hole exposing a double-bonded boron edge-atom. Due to having low knock-on energy threshold [5], this atom is ejected from the edge, leaving behind an unstable single-bonded nitrogen edge-atom. Ejection of nitrogen alternately leaves a double-bonded boron edge-atom, which is further ejected. Knock-on sputtering of the edge-atoms begins from such local steps and continues down the atomic row. This zipper-like knock-on mechanism is responsible in the rearrangement of the edges into a straight zigzag configuration in h-BN.

Our observations in Movies 2 and 3 are in good agreement with the recent study [7], predicting boron vacancy migration through its second neighbor. According to this prediction, boron vacancy migration occurs only above 840 K, while nitrogen vacancies do not show any mobility in h-BN. We observe boron vacancy migration in h-BN towards its neighboring vacancies. In this study, the electron beam is likely to provide sufficient energy for this migration. This migration is believed to reduce the surface energy of the film as the vacancies coalesce. This study does not show migration of isolated individual vacancies in the membrane under the electron beam.

Although it is not possible to track individual atoms at the step edges and vacancies, the atomic arrangements in each image here reveal the fascinating and complex interaction dynamics of the lattice atoms with the adatoms and molecules. It is not possible to identify the type of the adatoms diffusing along the step edges or at the point defects or lattice sites. However, we believe boron and nitrogen atoms at the edge reservoirs are strong candidates interacting with the vacancies. Carbon, hydrogen, oxygen and other light organic molecules are other strong candidates interacting with the edges and vacancies. Understanding such interaction dynamics is very important since it can help understand the functionalization mechanisms in h-BN and other two dimensional crystals [9].

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