Inelastic electron irradiation damage in hexagonal boron nitride

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Abstract

We present a study of the inelastic effects caused by electron irradiation in monolayer hexagonal boron nitride (h-BN). The data was obtained through *in-situ* experiments performed inside a low-voltage aberration-corrected transmission electron microscope (TEM). By using various specialized sample holders, we study defect formation and evolution with sub-nanometer resolution over a wide range of temperatures, between -196 and 1200 °C, highlighting significant differences in the geometry of the structures that form. The data is then quantified, allowing insight into the defect formation mechanism, which is discussed in comparison with the potential candidate damage processes. We show that the defect shapes are determined by an interplay between electron damage, which we assign to charging, and thermal effects. We additionally show that this damage can be avoided altogether by overlapping the samples with a monolayer of graphene, confirming this for h-BN and providing a way to overcome the well-known fragility of h-BN under the electron beam.

Keywords: hexagonal boron-nitride, inelastic irradiation damage, low-voltage TEM.

1. Introduction

The discovery of graphene [1] and subsequent graphene-analogues [2] has opened a new field of study regarding single-layered, quasi-2D materials. Transmission electron microscopy (TEM) has been used extensively in order to accurately describe their structure and chemical properties, down to the atomic scale, as shown in *e.g.* [3]. This has been partly made possible by the simultaneous advances in aberration correction [4, 5], which have allowed for better point resolutions and smaller probes.

In view of the poor resistance of these new materials to damage by the high-

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energy electrons, low (≤ 80 kV) accelerating voltages have been adopted as standard when characterizing them, taking advantage of the improved resolution due to aberration correctors. The atomically-thin nature of these materials makes them ideal samples for TEM, but at the same time requires large beam currents in order to obtain images with sufficient signal-to-noise (S/N) ratios. This is made even more problematic when requiring very high resolutions because the respective frequencies are dampened by the contrast transfer function (CTF) envelopes, further increasing dose requirements [6].

The result of these factors is an increase in the inelastic damage incurred by the sample. The processes through which this form of damage occurs are radiolysis [7-9] and charging [8, 10]. Unlike elastic knock-on displacements, this type of damage has a very low energy threshold and cannot be avoided by reducing the acceleration voltage. On the contrary, this leads to an increase in the inelastic cross-sections and thus to the damage rate [7-9]. For metallic materials (*e.g.* graphene), this damage is mostly avoided because electronic excitations are quenched rapidly and displaced electrons are replaced. The above argument does not hold for non-metals. As discussed in [11], the processes influenced by elastic effects are atomic displacement (either from the bulk or surface) and electrostatic charging. The first is excluded by our choice of operating voltage, while the second is affected only through the backscattering of incoming electrons and is of secondary importance in this process, which is dominated by electron-electron interactions. This leaves inelastic processes as the main source of specimen damage for these materials, when operating below the knock-on threshold.

In this paper, we report the results of our detailed study of inelastic damage in monolayer hexagonal boron nitride (h-BN). The data presented here has been obtained through a large number of *in-situ* experiments, using sub-threshold irradiation, at temperatures ranging from Liquid Nitrogen (LN₂, -196 °C) to 1200 °C. The first part of the paper presents a method that completely eliminates inelastic damage in h-BN by placing it on top (or under) a sheet of graphene. The second part presents the various defect geometries that appear while creating damage at different temperatures, which are in some cases completely different than the room- (or medium-) temperature ones. Finally, the last part of the paper quantifies the damage, allowing us to calculate cross-sections which are then discussed in relation to the various damage mechanisms.

2. Methods

The samples studied in this work were prepared by mechanically cleaving

commercially-available h-BN powder [12] or by using monolayer h-BN or graphene grown on Cu foil by chemical vapor deposition [13]. The flakes were subsequently transferred to either TEM grids or microelectromechanical systems (MEMS) heating chips.

High-resolution imaging and chemical analysis were performed using a Jeol JEM-2100F microscope, fitted with a cold field-emission gun, dodecapole-based aberration correctors (Jeol) and electron energy spectrometer (Gatan), operated at 60 and 30 kV [14]. Throughout the course of the experiments, the temperature of the samples was varied while inside the microscope, under vacuum, using either a LN₂ holder (Gatan, for low-temperature), a filament-based heating holder (Jeol, for intermediate temperatures) or a MEMS-based resistive heating holder (Protochips, for high temperatures).

The acquired data was processed using Digital Micrograph (Gatan). Additional processing was performed using ImageJ [15].

3. Results

Figure 1 summarizes an experiment involving a sample area that contains monolayer graphene and h-BN, as well as a region where the two overlap. The sample was oriented so that the h-BN was located at the beam-exit side. The same experiment produced identical results when repeated with a sample where the order of the materials was reversed. The overlap is visible in Fig. 1a due to the increase in intensity in the central region, which additionally features a Moiré pattern due to the rotational misorientation between the two materials. High-resolution images taken in regions “1”-“3”, corresponding to graphene, graphene-covered h-BN and h-BN respectively, are displayed in Fig. 1c-e. EELS spectra taken from the three regions, displayed in Fig. 1f, show the B, C or N edges and confirm our assignment.

In Fig. 1a, there is a striking difference between the graphene-containing regions “1” and “2”, which appear undamaged, and the pure h-BN region “3” which shows small defects and characteristic triangular-shaped large holes [16-18]. The region had already undergone several minutes of irradiation by the time the image was taken, in order to acquire the high-resolution and EELS data. The following 30min were used in order to attempt damaging regions “1” or “2” by scanning at high magnification, using large pixel times, or fixing the beam position on the sample. The amount of irradiation in region “3” was kept to a minimum. Despite these efforts, Fig. 1b, taken 30min later, shows an opposite outcome: regions “1” and “2” remained defect-free, while the

damage in the pure h-BN region “3” increased, both through the introduction of new small defects and enlargement of the existing ones.

In contrast to this behavior, we have seen exceptions where damage was created even in this type of sample by heavier contaminant atoms which etched small defects, while moving between various positions around the edges. This was however rare and required a source of contaminant atoms nearby (such as a larger agglomeration). When it did occur, the damage rate was much lower when compared to purely beam-induced damage in h-BN (discussed in detail below). In the case of samples with a low concentration of contaminants in the region of interest or when these were pinned down by existing edges and defects (such as the case in Fig. 1a), this type of damage did not take place.

Fig. 1 – (2 columns, color online) Irradiation damage in graphene and h-BN. (a, b) ADF-STEM Images showing the same region of a sample containing graphene, graphene-covered h-BN and h-BN, taken 30min apart. (c-e) High-resolution ADF-STEM images taken in regions “1”-“3” of (a). (f) EELS spectra acquired from regions “1”-“3” in (a); the B, C and N edges are arrowed. Data acquired using 60 kV electrons at 500 °C.

A second important phenomenon that we observed is the change in the shape of defects that are created in h-BN, under identical irradiation conditions, as a function of the sample temperature. The samples used for this part of the study contain only h-BN, without any kind of overlapping material such as *e.g.* graphene. This is illustrated in Fig. 2, which depicts four sequences of images, illustrating defect growth between 500 and 1200 °C. There is a striking difference between the 500 °C case (which displays the well-known triangular defect configuration), the 800-1000 °C cases (which show circular defect geometries) and the 1200 °C case (which displays hexagonal structures). An equivalent figure containing data acquired using 30 kV electrons is displayed as Fig. S1. This variation of the defect shape with temperature was consistent across experiments performed on several samples. In order to support this, additional examples of large defects created at different temperatures and different acceleration voltages, different than the ones displayed in Figures 1 and S1, are shown in Figure S2. The defects show the same show similar evolutions to the previous structures, highlighting the general nature of our conclusions. An important observation is that the temperature limits are not well defined and that the shape of the defect sometimes depends of the particular environment around the area. An example is given in Fig. S1, where at 650 °C a circular defect is formed. Other experiments under similar conditions have produced triangle configurations, showing that, especially in the intermediate temperature ranges, the evolution might be influenced by external factors.

Below 500 °C, in agreement with several previous reports [16-18], the larger defects have triangular symmetry, with N terminated edges aligned along the zig-zag direction. In order to test the limits of this hypothesis, we have created damage in h-BN at LN₂ temperatures. An example is shown in Fig. S3a, which displays an ADF-STEM image of a triangular defect created in a bilayer region, revealing the underlying monolayer. As shown by the intensity profile plotted in Fig. S3c, the ADF image allows distinguishing the atoms in the monolayer region and, considering the simple h-BN stacking, every atom in the image can be identified. Additional data regarding defect growth under these conditions, for a few-layer h-BN region irradiated at lower magnification, is displayed in Fig. S3d-f. This image sequence shows triangular defects

which maintain their shape and orientation as they grow under the electron beam. We conclude that, even under these extreme conditions, the damage is similar to the room- or medium-temperature case.

The values reported throughout this paper represent the “average” temperatures of the specimen holders, either monitored with the help of built-in thermocouples (Gatan and Jeol holders) or set with the help of existing calibration data (Protochips holder). The temperature increase due to the electron beam for our experimental conditions should be of the order of $\sim 1\text{K}$ [6], and thus negligible.

Fig. 2 – (2 columns, grayscale) Defect evolution in h-BN at various temperatures. Data acquired using 60 kV electrons.

An interesting aspect which we observed is that the edge orientation changes between the triangular and hexagonal defects. This is exemplified in Fig. 3, which shows a high-resolution image of a hexagonal defect, displaying edges that are oriented along the armchair direction. While the image resolves the edges directly, this is not necessary and the same information can be determined from the FFT, provided that at least the first set of h-BN lattice spots is resolved. By comparing the hexagon edges

with the inset FFT, we can see that the hexagon is aligned with the zig-zag spots, and thus perpendicular on the three armchair directions. Origins of this orientation change are discussed further in the discussion section below.

During our observation of a large number of hexagonal structures, we have seen that all follow the armchair-oriented edges rule with a single exception, which we show in Fig. S4 for completeness. Here, a h-BN bilayer damaged at high temperature forms a hexagonal defect whose sides are perpendicular to the zig-zag spots in the inset FFT. As this is the only case which was observed, its formation is difficult to explain; possible reasons include the environment surrounding the defect, the presence of an additional layer, or the slightly lower temperature compared to the typical hexagon formation.

Fig.3 – (1 column, color online) High-resolution image of a hexagonal defect in h-BN showing armchair edges. The FFT of the image is inset in the upper-right corner. Data acquired using 60kV electrons at 1200 °C.

In order to obtain quantitative data about the growth of defects at different temperatures, we adopted a model which takes into account the fact that defects expand via the removal of atoms from their edges. A cartoon is drawn in Fig. 4a, which indicates a defect whose radius increases from r_i to r_f during the time interval between t_i and t_f . Assuming uniform irradiation, the displacement rate p_{disp} at any given time is proportional with the number of atoms available at the edges, N :

$$p_{disp} = \frac{dN(t)}{dt} = N(t) \cdot \sigma \cdot j$$

, where j is the beam current density and σ is the single atom cross-section. The number

of atoms available at the edges is proportional to the perimeter:

$$N(t) = 2\pi r(t) \cdot \rho$$

, where ρ is the linear density of edge atoms. Combining the last two expressions produces a differential equation which allows the calculation of the cross-section through integration:

$$\begin{aligned} \frac{dr(t)}{dt} &= \sigma \cdot j \cdot r(t) \\ \rightarrow \sigma &= \frac{\ln(r_f/r_i)}{j \cdot (t_f - t_i)} \end{aligned}$$

The result is a simple expression which gives the average single-atom cross-section as a function of the intensity of the beam and of the initial and final properties of the defect. Two observations are in order: firstly, this formulation is general, and does not assume any specific damage model; secondly, even though the arguments here use a circular-shaped defect, the model holds for any regular polygon, as the perimeter is proportional to the radius of its circumscribed circle. We note, however, that the model is no longer valid if the defect shape changes with time.

The data obtained by using this model are plotted in Fig. 4b. The dataset contains 12 cases which were selected so that the evolution of the defect was visible in single-layered areas, far from impurities or obstacles, in order for the measurements to be significant. A beam current density j of $\sim 10^6$ e/nm²s was considered, which is typical for our experiments. Several conclusions can be immediately drawn. First of all, there appears to be little difference between damage rates at 30 and 60 kV. This indicates that the inelastic damage mechanism is the same under both conditions. Secondly, there seems to be an obvious difference between the behavior up to 1000 °C, which gives a cross-section of about ~ 20 bn and the one at 1200 °C which averages ~ 90 bn.

Additional information can be obtained by computing the average displacement rate, which has been calculated from the same dataset and is plotted in Figure S5. As expected from the previous results, this parameter is also approximately constant until 1000 °C at 1.17 at/s and then features a sudden increase. The total observation time for each defect is included as a label and gives an average of ~ 196 s. Combined with the displacement rate and the in-plane density of h-BN, this allows calculating an average surface increase of ~ 14.2 nm² during this time.

Fig.4 – (1.5 columns, color online) (a) Schematic model used for deriving the mathematical expression of the damage cross-section. (b) Temperature dependency of the calculated cross-sections, for two accelerating voltages.

4. Discussion

There have been several earlier qualitative studies of damage in h-BN, through TEM observations using 80 or 120 kV electrons at room temperature. Initially, several groups observed the formation of single-vacancies and larger triangular defects, having the same orientation [16-18]. By quantifying the direct images (through averaging) or the exit wave-function (EWF, obtained through focal-series reconstruction), the defects were determined to be N-terminated, in agreement with a higher knock-on displacement cross-section for B. A subsequent study highlighted an instance where a hexagonal defect formed in multilayer h-BN, under similar electron irradiation conditions [19]. Another report showed, through EWF studies, that the edges of the flakes had an equal probability of displaying B or N terminations, for both monolayer and multilayered areas [20]. A recent study has shown that the polarity of the defects which are created in h-BN depends on the temperature [21]; here it was found that at high-temperature N atoms are preferentially removed, creating N vacancies and B-terminated tetravacancies.

A detailed discussion of elastic electron-beam damage in h-BN is given in [22]. Using a static lattice model, the authors calculate the room-temperature threshold electron energy for displacing a B (N) atom from the pristine lattice at 80 kV (120 kV). The minimum energy for which displacements are still possible is calculated for atoms at the edges of larger vacancies at 40 kV (70 kV). It is interesting to compare the above with data for graphene, as detailed in [23]. Here, the authors predict an elastic damage threshold of 80 kV, but observe vacancy growth even at 20 kV, which sometimes progresses faster, showing that a metallic material such as graphene can also be affected

by the electron beam, even at this low acceleration voltage. The authors introduce an improved cross-section model which takes into account lattice vibrations, as well as the effect of temperature. The result of this model when applied to h-BN, using threshold energy values from [22], is plotted in Fig. 5. Several important consequences follow. Firstly, while there is a small difference between the high- and room-temperature cases, it does not change the damage hierarchy in this material, nor does it produce significant changes in the cross-sections, allowing us to conclude that elastic damage in this case is largely temperature-independent. Secondly, while this model features a gradual increase in cross-section and makes setting a threshold difficult, the values can be compared to the experimental ones and show that defects in this material cannot expand below 60 kV due to elastic damage, because of the N threshold. As such, any extended damage observed under these conditions is due to inelastic effects. Thirdly, it is interesting to examine the 80 kV case, where B atoms at the edges of larger vacancies have a cross-section maximum of ~ 60 bn, six times higher than for N. This shows that defects can evolve through elastic damage, with a preference towards the removal of B, which is seen experimentally [16-18]. Nevertheless, the elastic displacement of B atoms from the edges of larger vacancies cannot be neglected even at low accelerating voltages, especially in the case of high temperature. Lastly, the ~ 90 bn cross-section that we observe at 1200 °C cannot be explained even by the most optimistic predictions of this model.

Fig.5 – (1 column, grayscale) Knock-on displacement cross-section for various atomic positions in h-BN as a function of electron acceleration voltage, for different temperatures.

The overlap or encapsulation of samples by graphene has been shown to reduce electron-beam damage in the case of monolayer dichalcogenide samples [24, 25] or for graphene itself [26]. This has allowed images or spectral maps with better S/N ratios

and the observation of un-reconstructed defects, in regions of the sample which would otherwise transform under the beam. However, experiments using higher doses showed that in some cases the protecting layer itself damages, even when working at 60 kV under high vacuum conditions [24]. A possible mechanism for the initial vacancy creation is the chemical etching due to contaminants [23, 27]. Our results agree with this and show that graphene-covered h-BN samples also damage when imaging close to contaminated areas. This is illustrated in Fig. S6, which shows a triangle defect created by foreign atom etching in an area containing h-BN and graphene, at 600 °C. This damage mechanism is additionally supported by the irregular edges of the defect. EELS data (not displayed) shows that it is the h-BN layer which is etched away. Figure S6a shows a TEM image taken right after the defect formation, while Fig. S6b shows a STEM image of the same area taken 105 min later, with the electron beam away from the region between these two moments. A quick comparison shows that despite the high temperature, the shape of the defect remains unchanged. This proves that the electron beam is necessary in order for the chemical etching to take place, highlighting the fact that the reaction barriers cannot be overcome thermally at this temperature.

The observation of armchair edges in the case of hexagonal defects is surprising, but can be explained when taking energy considerations into account. Existing theoretical studies on h-BN nanoribbons [28-30] agree that armchair edges are the lowest in energy, and thus more favorable. There is therefore a discrepancy between this prediction and the zig-zag edges which are predominantly observed in TEM experiments. A possible solution is the difference between the thermodynamic and radiation stabilities for the various edge configurations. While this data is not available for h-BN, in the case of graphene a similar study has shown that there is an almost inverse relationship between the two, leading to non-trivial variations as a function of both temperature and irradiation conditions [31]. Considering the lattice symmetry of h-BN, a reconstruction of the edges along the armchair direction necessarily transforms any circular-shaped defect into a hexagon. As the irradiation conditions do not change, this effect must be caused by the increased temperature, supporting the idea of a balance between inelastic damage and thermal effects.

The two inelastic mechanisms that could be responsible for the sub-threshold h-BN damage are radiolysis and charging. Radiolysis results in atomic displacements due to electronic excitations. It has been treated in detail by Hobbs [7, 8], which defines several criteria that are necessary in order for this mechanism to function. Briefly, it requires localized electronic excitations which must be stable for long enough for the nuclei to respond mechanically (~1 ps) and which must have energies comparable to the

displacement threshold. Inner-shell electron excitations carry sufficient energy, but usually decay via X-ray or Auger emission too quickly to affect the nucleus [7]. Excitons in h-BN satisfy the localization and lifetime criteria [30] but fail the last one, as their ~6 eV energy [33] is lower than the 8.6 eV (13 eV) minimum threshold for B (N) [22]. Additionally, an energy-to-momentum conversion mechanism, required in order to transfer the exciton energy to the atom cores, has not been documented for this material.

Lastly, specimen charging occurs in the TEM because of the emission of secondary and Auger electrons, which leaves the sample positively charged. In the case of insulating samples such as h-BN, this charge cannot be compensated by the surroundings. This phenomenon has been studied by Hobbs [8] and Cazaux [10]. There is a strong contrast between the behavior of thick specimens in the SEM, which absorb part of the incoming electrons and acquire a negative charge and the thin TEM foils, for which all of the incident electrons emerge from the opposite side. According to Hobbs [8], the positive charge creates a potential which prevents further electron emission. The electric field affecting the region has an equilibrium value which reaches a maximum at the edges of the irradiated area of $\sim 10^8$ V/m under our experimental conditions. Since this is similar to the dielectric breakdown strength of h-BN [34], there is a possibility that this field is strong enough to destroy the irradiated region.

An alternative to the above is to balance the excess charge by ejecting positive ions from the sample. This scenario is explored by Cazaux [10], which establishes an equilibrium relationship between the number of emitted electrons and the necessary ion current. Using his expression, we can calculate an expected loss of ~1 at/s under our conditions. This value can be compared with those plotted in Fig. S5, which have been calculated from the same dataset used in Fig. 4. Here, an average value of 1.17 disp/s is obtained for temperatures up to 1000 °C, which provides an excellent agreement. Although difficult to quantify in the absence of an exact model, the difference in binding energy between B and N edge atoms and the pristine lattice suggests that the ejection rate of the former should be higher [8, 9], resulting in N-terminated structures with a similar polarity to those created under knock-on conditions.

There is a significant increase in the displacement rate (and cross-section) at 1200 °C, which points to a change in damage mechanism under these conditions. An important issue is the possibility of chemical reactions between the edge regions and impurities. Persistent impurities at the defect edges were excluded using a combination of ADF-STEM imaging and EELS spectroscopy. In particular, EELS data acquired from the edge regions of the hexagonal defects, at high temperature, indicate only the B and

N edges, without any C signal. A further possibility is given by vacuum residuals. Verifying this is made difficult by the fact that it is impossible to measure the composition of the residual gas surrounding the sample. There are several alternatives for testing this hypothesis, all of which are beyond the limits of our experimental setup: firstly, the same experiments could be performed in a microscope where the environment can be better controlled. This could either be a machine with better sample-area vacuum or one where various gasses can be introduced in a controlled way. Secondly, any temperature-related effects should display an Arrhenius-type exponential temperature dependency, which should be visible at temperatures beyond the 1200 °C limit of our MEMS holder. Indeed, the near-constant displacement rates up to 1000 °C underline the fact that these effects dominate only at very high temperatures.

Covering the h-BN samples with graphene reduces damage by providing a continuous source of electrons to replace the ones that have been lost due to electron irradiation. Combined with the absence of damage when the electron beam is not present in the area, this strongly points to charging as the main inelastic damage mechanism in this material. This is reinforced by the good agreement between expected and calculated damage rates. The other important factor which plays an important role on defect evolution is temperature. The change in defect shape and damage speed indicates that the growth of the defects is influenced by temperature through edge reconstructions and/or local chemical reactions with the vacuum residuals. These effects dominate over 1000 °C and produce values which show strong deviations in our dataset.

5. Conclusions

To summarize, we have shown that inelastic electron irradiation damage in h-BN functions over a wide range of temperatures, which influence the geometry of the defects produced and allow control over their configuration at the atomic scale by changing the environment conditions. By quantifying and analyzing the defect evolution, we have concluded that the mechanism responsible for this damage is charging, which is not unexpected in a case of an insulating material such as h-BN. Finally, in support of our hypotheses, we have shown that inelastic damage in this material can be prevented when overlapping it with a monolayer of graphene, opening the way to measurements which involve high electron doses, such as spectroscopy. Our findings shed light on the factors which control the evolution of this material under the electron beam and provide solutions which should encourage further work.

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