High Angle Dark Field Imaging of Two-Dimensional Crystals

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Abstract. Two-dimensional (2D) materials, graphene, hexagonal boron nitride (h-BN) and transition metal dichalcogenides (TMD) have been investigated by means of Scanning Transmission Electron Microscopy (STEM), in particular via High Angle Annular Dark Field (HAADF) imaging technique. They are compared in terms of their structure and durability under intense electron beams.

1. Introduction

Graphene and other 2D nanomaterials have attracted considerable attention since their isolation due to their unique physical, chemical, and structural properties as well as their great potential for applications 1. Single-layer h-BN is one such material whose wide band gap of ~5.9 eV arguably makes it the thinnest possible insulator and therefore a perfect candidate for incorporation into complex heterostructures consisting mostly of low-dimensional materials 2. Owing to the unique properties of h-BN, much effort has been put into exploring its potential use in electronic and optoelectronic devices such as field emitters and ultraviolet or radiation detectors 3. It has also been recently found that h-BN is a much better substrate (inert) for graphene studies than SiO2 as it improves the graphene electronic properties 4. Other technologically important 2D materials, TMDs e.g. molybdenum disulphide (MoS2) and tungsten disulphide (WS2), are also under heavy investigation as a new class of materials with remarkable properties 5. Single layer TMDs with a thickness of 6.5Å have a direct band gap contrary to their bulk forms which have an indirect band gap. By implementing these layered materials into graphene based devices (by stacking them on top of each other), the device performance can be enhanced 6. Although electrical, magnetic and mechanical studies of 2D materials and their combination as new material systems are established, there is a lack of direct atom-by-atom visualizations, thus limiting our understanding of these highly exciting material systems.

Here we present a STEM study, in particular via HAADF imaging of graphene, h-BN, MoS2 and WS2, which we have used extensively in the past years. The location and nature of individual atoms, defects and peeling thick regions of 2D crystals layer by layer under an intense electron beam will be discussed.
2. Experimental

Two different sample preparation techniques have been employed to fabricate our 2D crystals. The chemical vapor deposition (CVD) technique for graphene and the micromechanical cleavage technique for h-BN, MoS$_2$ and WS$_2$ have been used. To prepare CVD-graphene films for the microscopy measurements, the films were initially coated with PMMA followed by etching of the copper substrate, on which graphene was grown, in ammonium persulphate solution. The other 2D materials were ‘peeled’ several times from their bulk crystals using adhesive tape and then placed onto an oxidized silicon wafer (Si/SiO$_2$). Thin flakes consisting of single up to many layers were identified under the optical microscope, coated with PMMA and transferred to a quantifoil TEM grid, after having etched-off the Si/SiO$_2$ substrate. The PMMA layer was then dissolved by dipping the grid into an acetone for about 15 minutes and then drying the samples in a critical point dryer to avoid possible sample damaging due to surface tension.

Preliminary studies (location and identification of the layers) of 2D crystals have been performed in a conventional TEM, however, detailed structural and topographic properties have then been studied in an aberration corrected STEM (Daresbury SuperSTEM). The structure, individual atoms and defects in the samples have been directly revealed in HAADF images, which show $\sim Z^2$ sensitivity. The STEM was operated at 60 keV, which is known to be ‘safe’ (below the knock-on threshold damage) for all studied materials according to the ab-initio calculations for all B, C, N, S, Mo and W.$^8,9$

3. Results and Discussion

Figure 1 shows raw STEM-HAADF images of single layer graphene at different magnifications. The reasonably large area of graphene in fig. 1a) shows the single layer is not perfectly clean. Residue free (clean) graphene regions are limited in size (from few to few hundred nm$^2$) and surrounded by contamination, which was found to consist of C, O and Si in our EDX analysis. These hydrocarbon contaminations appears bright due to higher scattering with heavier atoms and larger thickness, however, clean graphene areas are dark. Moreover, due to different thickness of hydrocarbon layers, their brightness in HAADF image appears from grey to very bright, shown in fig. 1b). On the other hand, to be able to see individual carbon atoms and periodicity a closer look is required. Although it is an unprocessed image, the carbon atoms and hexagonal periodicity of the graphene are clearly visible in fig. 1c). Carbon atoms are bright and holes dark in the image in fig. 1c) and benzene rings are overlaid in red highlighting the hexagonal periodicity.

![Figure 1](image_url)
Due to its weak contrast on oxidized silicon wafers compared to graphene and other 2Ds, obtaining and identification of single layer h-BN via optical microscope is quite challenging. Double layer h-BN STEM-HAADF images are presented in fig. 2a). The intensity of both, B and N atoms is low similar to carbon in graphene but they are discernible in HAADF image due to the $\sim Z^2$ sensitivity. Although theoretical calculations predict that the knock-on threshold for h-BN should lie above the beam energy used for this study, 60 kV, we found that there is considerable damage inferred to pristine h-BN. As a result, thicker regions of the h-BN flakes can be peeled layer-by-layer under the beam, which conveniently exposes a different number of layers and helps in determining the stacking configuration. An HAADF image of a 'beam-exfoliated' region is shown in fig. 2b), where a single layer patch with triangular shape appears in the middle of the image, surrounded by the original double layer sheet. It is known that h-BN damaging leads to the formation of triangular holes in single layer h-BN sheets\textsuperscript{10}, Fig. 2c) is the noise filtered image of fig. 2b) and shows improved visibility of the B and N sites in the h-BN sheet. This allows better differentiation between B and N, and is further demonstrated by drawing an intensity profile (inset) along the line in the triangular feature. The intensity ratio between N and B in fig 2c) is found to be 1.91, which is compatible with the $Z^2$ ratio of 1.96.

![Figure 2](image)

**Figure 2.** Atomic resolution raw STEM-HAADF images of (a) double layer h-BN, (b) the triangular appearance of single layer h-BN as a result of electron beam etching of the double layer, (c) filtered image of (b). B and N can be distinguished by their intensity in the profile (inset) across along the line in the ‘triangle’ (c).

Single layer MoS\textsubscript{2} consists of two distinct sub-lattices: Mo (metal) atoms are trigonal-prismatically bonded to pairs of S atoms and arranged hexagonally in a plane. The resulting S-Mo-S slabs are then stacked in various sequences, 2H stacking being the most common. Similar to graphite and h-BN, chemical bonds within the plane are covalent (strong) while weak van der Waals bonds are established between stacked layers to form a bulk (3D) crystal. Figure 3 illustrates how damage initiates immediately: the image in fig. 3b acquired approximately 30 s after that in fig. 3a) demonstrates the ease with which damage is introduced. The single-layer MoS\textsubscript{2} is perforated by losing first a single S atom and then the Mo-bonded S atom resulting in the formation of a vacancy \textsuperscript{9}. As can be seen in fig. 3c), the vacancy is soon turned into a hole (after $\sim$ 1min), which enlarges easily under the scanning electron beam. This is mainly due to the atoms at the edge of the hole being less coordinated with fewer/weaker atomic bonds thus facilitating both ionization and knock-on damage. Furthermore, the sputtered atoms during the damaging behave differently from those in graphene and h-BN in which atoms were knocked-out and lost from the area. However, here the sputtered Mo atoms tend to accumulate at the edge of the hole revealing themselves by extra brightness in the HAADF image in fig 3c). This is probably due to higher atomic weight of Mo, which requires higher displacement...
energies. EDX analysis (not shown) confirms that the brighter edges are rich in Mo rather than S. This is also the case for single layer WS$_2$, as is revealed by the decorated edge around the hole in fig. 3d), which is rich in W. The electron dose used in these images was $\sim 5 \times 10^6$ e/Å$^2$, which is similar to what we used to acquire other 2D.

Figure 3. Atomic resolution HAADF images of pristine single layer MoS$_2$, a) before and b) after consecutive scans, showing vacancy formation; c) expansion of the damaged region; d) damaged single layer WS$_2$. All images are raw.

4. Conclusions

In conclusion, we have prepared samples of free standing graphene, h-BN, MoS$_2$ and WS$_2$ via different techniques and analyzed by aberration corrected STEM at 60 kV. We were able to observe individual carbon, boron and nitrogen, molybdenum and sulfur as well as tungsten and sulfur atoms in the graphene, h-BN, MoS$_2$ and WS$_2$ lattices, respectively in HAADF images. However, employing a 60-kV acceleration voltage of the electron beam and near-UHV conditions (<5×10$^{-9}$ torr in the column) did not prevent occurrence of damage in free-standing 2D crystals, except for graphene, either due to knock-on or ionization damage. This indicates the need for application of protective measures to 2D during prolonged microscopy analysis, such as graphene encapsulation.

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