

DEFENSE THREAT REDUCTION AGENCY FINAL REPORT

Project Title: Ion Irradiation Effects in Graphene
Electronics for C-WMD

Grant/Award #: HDTRA1-12-1-0013

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Project Summary

In this project we have investigated the sensitivity of graphene and 2D material-based electronics to ion-beam irradiation using high resolution transmission electron microscopy, combined with electronic transport measurements. In this single scope study we have developed and employed a range of advanced electron microscopy techniques in order to understand the irradiation induced changes in structure and properties graphene and other 2D material-silicon hybrid devices.

The work has been underpinned by advanced transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) characterization of 2D materials and their integration in electronic devices. STEM characterization is traditionally performed by plan view imaging of suspended 2D materials. Here we have extended this approach by imaging within a specialist TEM capable of performing ion irradiation while simultaneously imaging with electrons. Our in situ ion irradiation experiments have demonstrated that graphene's atomic structure is surprisingly robust to ion irradiation and is even able to heal structural defects when there is a local source of carbon such as from polymeric residue. However, we find a critical ion fluence where the long range order of the structure is lost and where the electronic properties transform from conducting to insulating.

We have shown that graphene's electronic performance is improved by encapsulation with boron nitride – which has lead to the current generation of high performance graphene electronics incorporating vertical heterostructure stack geometries. In this project we have pioneered the development of atomic resolution STEM cross sectional imaging for understanding the full integrated structure of many 2D material / graphene hybrid devices. This is now an essential characterisation approach which is enabling the advancement of 2D materials for a wide range of applications including spintronics, water filtration, quantum communication, optics and tritium production.

During the later stages of the grant the project was extended to address the radiation behavior of some of the new generation of 2D materials, many of which are unstable in air. The collaborations initiated with this grant between the PI and CoIs has allowed irradiation damage studies to be performed on the latest generation of emerging 2D materials in the most timely manner possible. For example, we have shown the first evidence of the structure of irradiation induced atomic point defects in NbSe₂, InSe and GaSe, with important implications for their superconducting and optoelectronic properties, respectively. In addition, we have harnessed the acquired knowledge of irradiation damage to demonstrate lithographic patterning of graphene heterostructures with ~3nm resolution, considered to be an essential step to harnessing graphene and black phosphorus for high speed electronics.

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1. Introduction

The DTRA's \$750,000 investment has allowed us to develop a quantitative understanding of the irradiation behavior of various 2D materials and their heterostructures, including graphene, boron nitride, black phosphorus and niobium diselenide. The research has generated an exceptional volume of high quality research outputs, with 42 peer reviewed publications including the highest impact factor journals (2 in Nature, 1 in Science Advances, 1 in Nature Nanotechnology, 2 in Nature Materials, 8 in Nano Letters, 4 in Nature Communications, 4 in ACS Nano, 1 in JACS). It has also aided in the promotion of the PI from lecturer to full professor, and supported 5 PhD students and 4 postdoctoral researchers at a crucial early stage in their career.

The following report describes the key results achieved over the 5 years of the project with the full results and raw data having been already published as peer reviewed journal outputs and the majority are freely available to the public (gold open access). All publications are also freely available from the PI if required, please contact sarah.haigh@manchester.ac.uk.

2. Background

Graphene-silicon hybrid devices offer exciting opportunities for next generation electronics (smaller, faster, flexible, transparent), terahertz devices and quantum computation beyond the limits of silicon technology. The potential of this new technology has driven funding agencies around the world to recognize the necessity of substantial investment in graphene-silicon hybrid technology. US Defense is estimated to have invested more than \$15M/year since 2008 towards understanding the fundamental physics of these devices (including: "Carbon electronics for Radio Frequency Applications" \$30M, DARPA; "Fundamental Graphene Material Studies and device concepts" \$7.5M, US Air Force; "Tailoring Electronic bandgap of nanostructured graphene", US Navy, \$7.5M)¹. These new technologies have many defense-critical applications, including improved communications, sensors, navigational/avoidance systems in automated weapons or military aircraft. However, before the start of this project almost nothing was known about whether these materials will continue to function effectively when exposed to harsh environments such as high altitude reconnaissance and in close proximity to nuclear threats. The aim of this project was therefore to address this lack of understanding so that new high performance graphene-based electronics are able to be deployed safely in defense applications. Only if the mechanism and parameters effecting radiation stability are understood and quantified can strategies for the design of radiation-hard devices be proposed and safe operation be assured. Over the duration of this project new 2D materials, such as transition metal dichalcogenides (TMDCs) and monochalcogenides, emerged with great potential in defense applications such as high speed communications and sensors. The team therefore expended their efforts to investigate irradiation effects in 2D materials silicon-hybrid devices beyond graphene.

¹ Scott Dudley, "Graphene: a US military funding perspective" Accessed 26th October 2014
http://ec.europa.eu/research/industrial_technologies/pdf/graphene-presentations/4-4-dudley-22032011_en.pdf

3. In situ Ion irradiation of suspended graphene

1.1 Successful demonstration of the first ion irradiation studies of suspended graphene with observation of the resulting microstructural changes using in-situ transmission electron microscope (TEM) imaging.

The team fabricated few-layer and many-layer graphene sheets using mechanical exfoliation and transferred these to TEM support grids. The grids were irradiated using the MIAMI irradiation facility (University of Huddersfield, UK) to expose the materials to 30 keV He and Ar ions while simultaneously imaging in-situ within the TEM. Dislocation networks and kink band defects have been found in irradiated few layer graphene samples but the mechanism of formation was highly controversial. By direct high resolution TEM imaging of microstructural changes occurring during ion beam irradiation our results have demonstrated vital information regarding the dynamics of radiation induced structural changes in graphene sheets. We have shown that there is a whole sequence of structural changes (Figure 1) initiated by dislocation injection at grain boundaries [as reported in our paper Hinks et al Carbon 2013]. The plan view TEM micrographs in Fig. 1a–d show the structural changes observed in a single crystal of graphite during the in situ experiments with cross sectional schematics to illustrate the process. The TEM images were extracted from video captured during continuous ion irradiation which allowed the evolution of this dynamic system to be recorded.

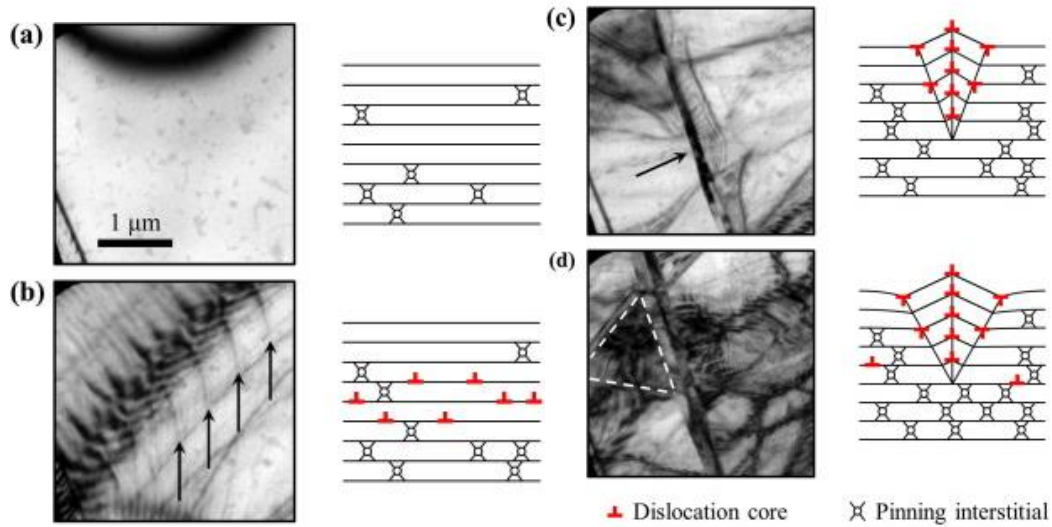


Figure. 1. Radiation induced structural modification and evolution in a thin single crystal of graphite observed perpendicular to the basal planes via TEM during in situ ion irradiation with 60 keV Xe⁺ ions at room temperature: (a) virgin sample before ion irradiation; (b) an irradiation-induced dislocation array (indicated by black arrows) at a fluence of 1.2×10^{13} ions cm^{-2} ; (c) immediately after the creation of kink bands (example indicated by black arrow) at a fluence of 1.4×10^{13} ions cm^{-2} ; (d) at the end fluence of 3.0×10^{13} ions cm^{-2} showing the 60° orientation relationship between kink bands (indicated by dashed white equilateral triangle); (a)–(d) schematic diagrams illustrating the evolution of the microstructure viewed parallel to the basal planes. The micrographs show the same area of the sample and the scale marker in (a) applies to all four micrographs.

These results show that even large structural defects like kink bands may be prevented by eliminating grain boundaries from the material. Consequently we believe that graphene-silicon devices will be more radiation hard simply through the use of single crystal graphene rather than polycrystalline films. The ion irradiation we observe produces significant strain within the structure the presence of which can be measured using Raman spectroscopy [as described in our paper Gong et al, ACS Nano 2013]. Our more recent work has shown that the types of irradiation induced microstructural defect produced can be predicted by knowledge of the material thickness and ion fluence (see later section).

1.2 The first atomic resolution scanning transmission electron microscope (STEM) characterization of 2D amorphous structure resulting from ion irradiation.

The team have prepared large area suspended monolayer graphene sheets on transmission electron microscope (TEM) support grids and irradiated these in-situ within the TEM using 30keV He and Ar ions. We have used Raman spectroscopy to quantify the irradiation dose and our experiments have revealed the unexpected result that single-crystal monolayer graphene is structurally stable for relatively high ion dose (Figure 2). In fact no damage was observed up to 10^{12} ions/cm². Instead above a critical dose, the graphene rapidly undergoes a striking change as the perfect hexagonal lattice transforms to an amorphous 2D structure. The structure was investigated by electron diffraction and high resolution scanning TEM (Figure 3, reported as Pan et al, Scientific reports 2014).

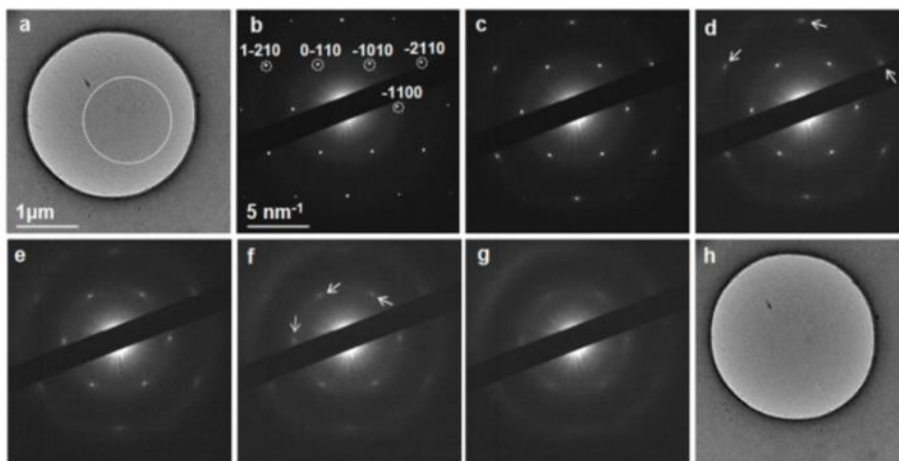


Figure 2 : Electron diffraction patterns recorded in-situ for single-layer graphene as a function of 30 keV He ion irradiation. (a) BF TEM image and (b) electron diffraction pattern for the single-layer graphene sheet before ion irradiation. (c)–(g) Show a sequence of selected area electron diffraction patterns acquired during in-situ irradiation of the single-layer graphene sheet with 30 keV He ions after fluences of (c) 3.0×10^{15} ions cm⁻², (d) 6.0×10^{15} ions cm⁻², (e) 9.6×10^{15} ions cm⁻², (f) 9.9×10^{15} ions cm⁻² and (g) 1.2×10^{16} ions cm⁻². Selected area region used to acquire diffraction data (b)–(g) is indicated by the dashed circle in (a). (h) BF TEM image after 1.2×10^{16} ions cm⁻² of irradiation. Reproduced from Pan et al Scientific reports 2014.

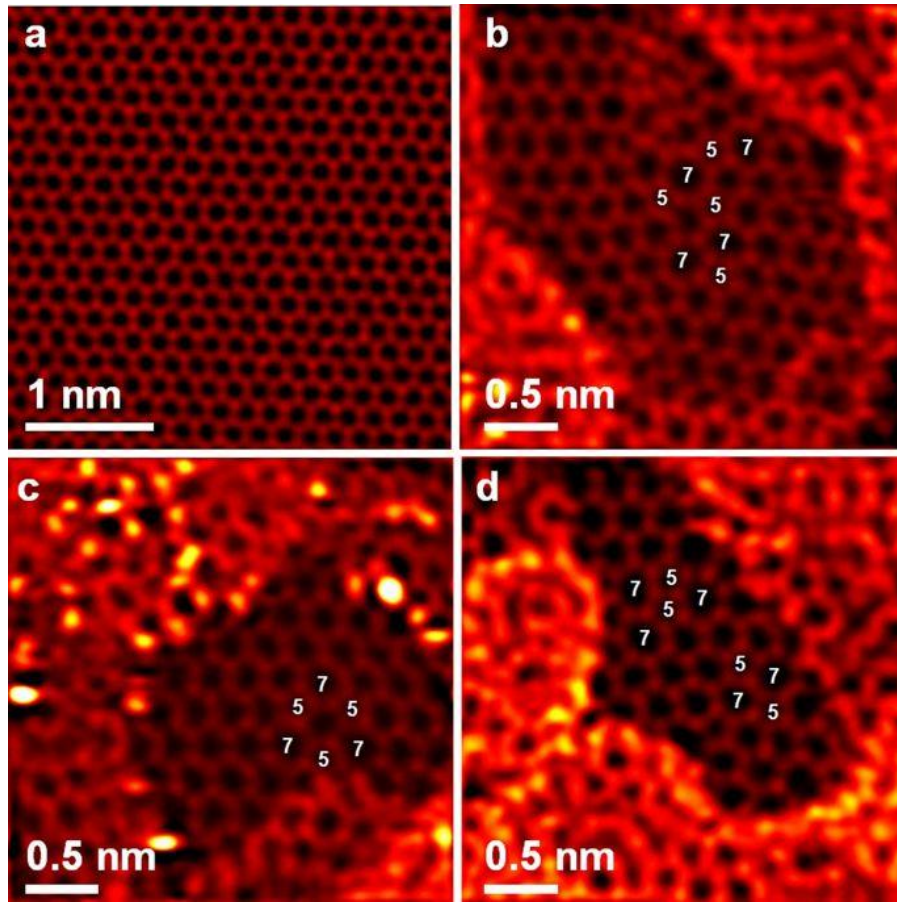


Figure 3: Atomic resolution HAADF images of single-layer irradiated graphene. (a)–(d) Filtered atomic resolution HAADF images of single-layer irradiated graphene (30 keV He ions) at fluences of (a) 3.0×10^{15} ions cm^{-2} and (b)–(d) 9.6×10^{15} ions cm^{-2} . Bright spots in (c) are heavy atom contaminants (most likely silicon or metal atoms). Pentagon-heptagon (5–7) pairs, a unit cell of the haeckelite structure, Stone-Thrower-Wales defects and Inverse-Stone-Thrower-Wales defects are observed in (b), (c) and (d), respectively. Reproduced from Pan et al Scientific reports 2014.

4. Understanding irradiation damage in graphene-boron nitride vertical heterostructures

4.1 First Cross Sectional TEM imaging of graphene-BN vertical heterostructure silicon devices

A vital prerequisite for our study of ion irradiation induced structural damage in graphene-silicon hybrid devices was the ability to successfully prepare pristine undamaged electron-transparent cross sections.

We demonstrated the first successful fabrication of graphene-silicon device cross sections suitable for TEM imaging using focused ion beam (FIB) milling procedures in 2012 (as published in Haigh et al Nature Materials, 2012, 533 citations). This required optimization of milling routines in order to ensure the correct region of the device was examined and that the ion milling did not damage the device during sample preparation. High resolution TEM and STEM imaging of these structures revealed the highly unexpected result that these multilayer structures are not simply composites stuck together by amorphous regions of polymer transfer residue but are in fact perfect artificial crystals with atomically flat clean interfaces. This discovery has paved the way for production of a huge range of engineered heterostructures based on vertically stacked 2D sheets (as discussed in Geim and Grigorieva, Van der Waals heterostructures, Nature 499 (7459), 419, 2013). The importance of this discovery is demonstrated by the more than 4600 citations received by this paper to date (almost 1000 per year!).

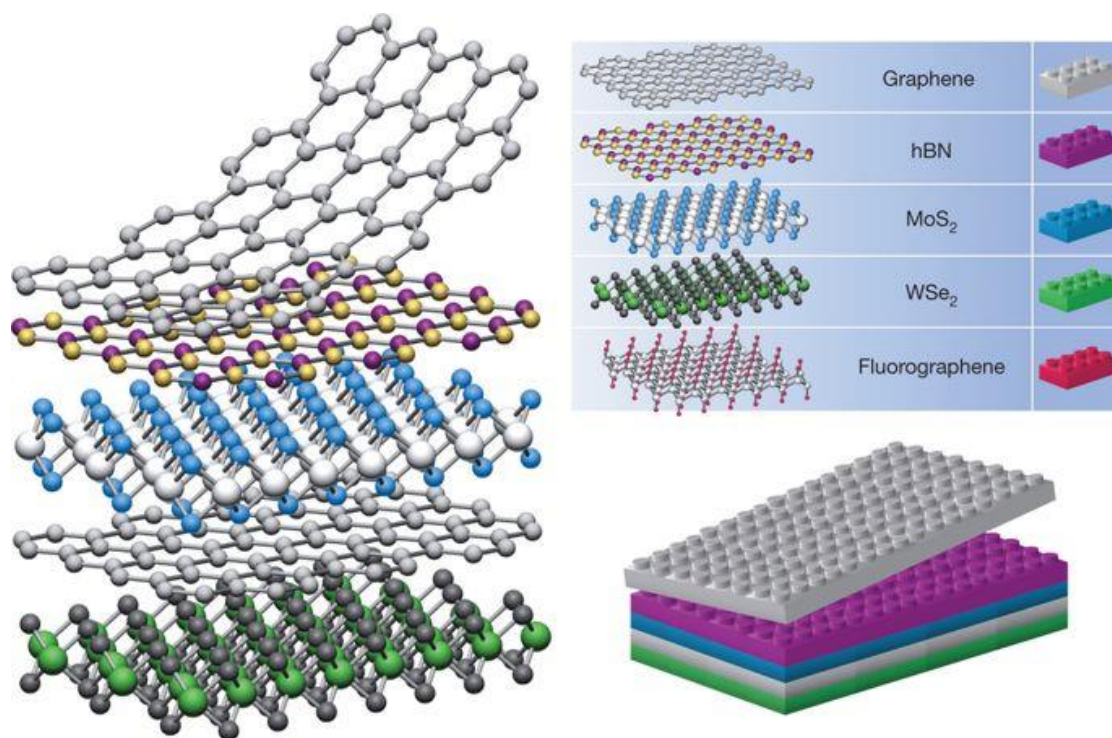


Figure 4: Building van der Waals heterostructures. If one considers 2D crystals to be analogous to Lego blocks (right panel), the construction of a huge variety of layered structures becomes possible. Conceptually, this atomic-scale Lego resembles molecular beam epitaxy but employs different ‘construction’ rules and a distinct set of materials. Reproduced from Geim and Grigorieva, Van der Waals heterostructures, Nature 499 (7459), 419, 2013

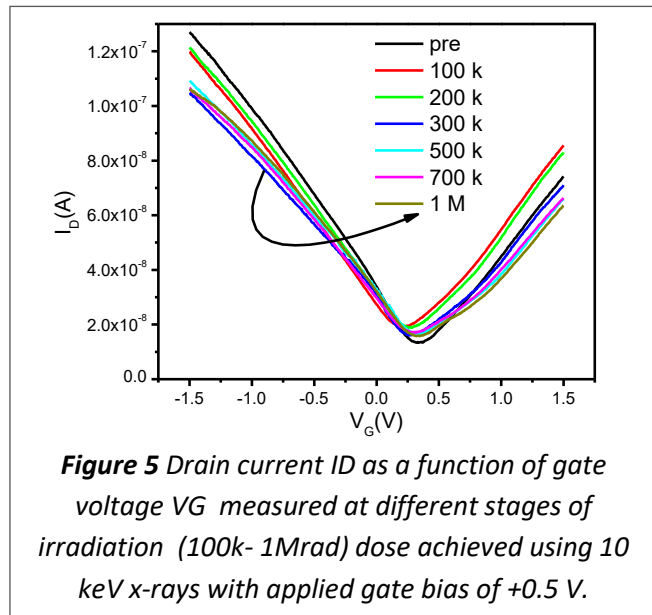
4.2 Correlation of transport properties with atomic layer roughness

Imaging of the individual graphene layers at the atomic scale has revealed that some layers are ‘flatter’ than others. Comparison with the mobility of the graphene layers measured ex-situ revealed a correlation between the atomic layer roughness and the mobility, with rough layers having lowered mobility. This explains why graphene sandwich structures (where the graphene sheet is encapsulated between two boron nitride (BN) sheets) have been shown to have better performance than identical

unencapsulated structures (as published in Haigh et al Nature Materials, 2012, 533 citations). This improved understanding has led to a revolution in graphene device fabrication with a much greater emphasis on vertical sandwich type structures and fast switching devices having an additional upper BN layer, for example see our publications Georgiou et al Nature nanotechnology, 2013 (1151 citations) and Withers, et al Nature materials, 2015 (723 citations) . Our in situ ion irradiation experiments have demonstrated that graphene actually appears to get macroscopically flatter when ion irradiated, which might be expected to lead to an increased mobility. However, this effect is found to be mitigated by changes to the local electronic environment which dominate the irradiation induced electronic behavior (discussed in section 4.3).

4.3 Measurement of irradiation induced shift in Dirac point for encapsulated graphene devices

After the 2013 DTRA conference we established collaboration with Prof Alles at Vanderbilt to take advantage of his capabilities for in-situ ion and 10 keV X-ray irradiation with simultaneous electrical transport measurements. In situ results from these Graphene-BN-Graphene-structures have been published (Zhang et al Radiation effector on encapsulated graphene-hBN devices, IEEE Journal of nuclear Materials 2014). Interestingly, the Dirac point of the device was found to shift slightly negatively at low radiation doses (evidence of hole trapping), and then shifts positively (evidence of negatively charged interface defects) for higher dose exposures up to 1 Mrad (SiO₂).

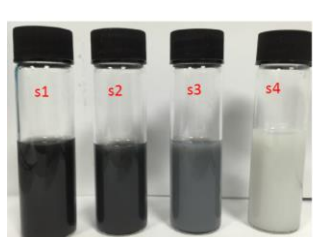


X-ray irradiation studies are limited to ionization effects. However, the 2D nature of the components in our devices renders them particularly vulnerable to failure by knock-on damage. To study this we also planned to investigate the effect of high energy ions on electrical response in collaboration with Vanderbilt but unfortunately none of the six graphene devices transported survived long enough for this to be completed. These prototype graphene devices are highly sensitive, making them difficult to test and transport especially for those unused to handling the devices.

4.4 Exploring the effects of high energy alpha irradiation on graphene BN heterostructures

Replicating damage from high energy light ions is difficult due to their small damage cross sections, particularly for low atomic number materials such as graphene and BN. However, Manchester's pelletron accelerator has been designed to allow high ion fluxes to be achievable. We therefore used the newly commissioned 5 MV NEC 15SDH-4 tandem pelletron ion accelerator, equipped with a toroidal volume ion source (TORVIS) at the Dalton Cumbrian Facility, U.K which is capable of light element ion irradiation studies at much higher energies than was previously possible (0.5-10 MeV).

We completed 3 visits each of 5 days duration to test the effects of high energy alpha irradiation by performing measurements at the University of Manchester's new pelletron accelerator at the Dalton Cumbrian Facility. We took three different types of samples to this facility in order to allow correlation of observed structural changes with the electrical response. In contrast to previous studies which have studied graphene in isolation, we are particularly interested in the effect of different ratios of graphene:BN. The samples we studied therefore comprised suspended graphene-BN heterostructures prepared on TEM compatible grids and graphene-BN heterostructures with different quantities of BN:graphene on oxidised silicon substrates. The films are made by dropcasting graphene and hBN inks onto silicon wafer and allowed to dry (see figure 6). This creates thin films analogous to state of the art devices, but which are comparatively fast to synthesis and provide a larger area for analysis.



Sample Name	s1	s2	s3	s4
Gr : BN	100: 0	90: 10	50:50	10:90
Initial Gr Conc.	3mg/ml	2.74mg/ml	1.5mg/ml	0.32mg/ml
Initial BN Conc.	-	0.30mg/ml	1.55mg/ml	3.28mg/ml
PS1 Conc.	0.31mg/ml	0.31mg/ml	0.30mg/ml	0.29mg/ml
H2O Volume	10ml	10ml	10ml	10ml

Figure 6 : Preparation of solutions used to create thin films with different graphene-BN ratios (used for ion irradiation experiments at DCF).

Stopping Range of Ions in Matter (SRIM) calculations predicted that it would take 8 hours of beam time to achieve the 1 dpa target in our stacks at a current of He²⁺ (alphas) with an ion beam energy of 0.5 MeV and a beam current of 10mA. However, in practice achieving this beam current was highly challenging and was limited to 1mA, giving a dpa of 0.2mA achieved over 4 days of beam time. A repeat visit was recently performed where it was possible to increase the damage to ~0.5 dpa in some samples. Our subsequent SRIM calculations (Figure 7E) suggest that the damage cross section should be uniform throughout the samples due to their small thickness.

Ex-situ optical and scanning electron microscopy characterization reveals inhomogeneous damage to the film, with damage concentrated in circular areas (Figure 7). Damage to both the film and the silicon substrate are very evident, the latter is possibly due to enhanced vacancy production ~6μm subsurface at the limit of the incident proton range. Hydrogen bubbles form in the film (see Figure 7 D), possibly aggregating and giving way to circular absences. These results point to the requirement of a radiation

resilient substrate which can also function as a back gate electrode for novel graphene-based devices in hazardous environments.

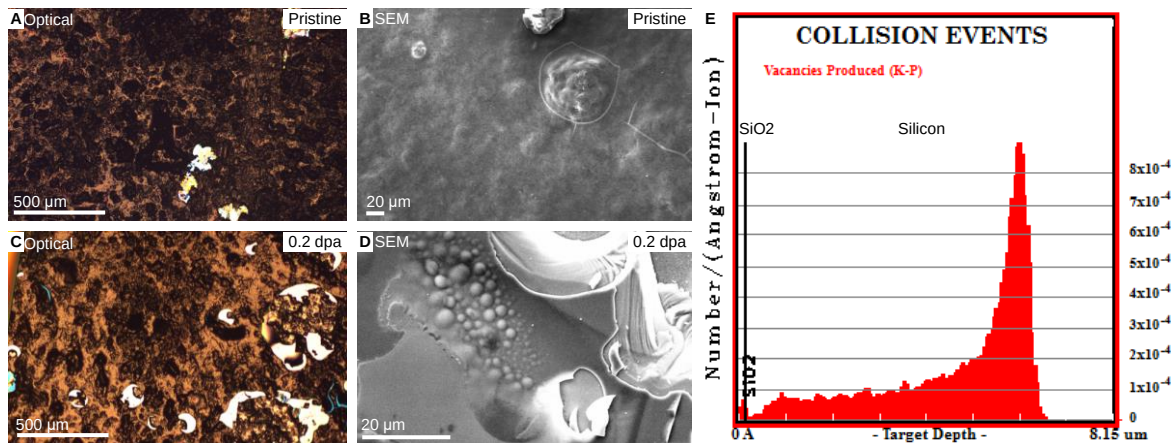


Figure 7: A, B, Optical and scanning electron microscopy (SEM) images of pristine graphene/hBN films. The films have a rough morphology and cracks can be seen in the SEM image. C, Optical microscopy image of film damaged to ~ 0.2 displacements per atom (dpa). The surface is still rough and bright circular regions have appeared. Further inspection of the film by SEM (D) reveals the bright regions are exposed silicon wafer where the film has been degraded. Close to these regions helium bubbles can be seen. The silicon wafer has also suffered heavy damage, which is probably due to an enhanced vacancy concentration at $6\mu\text{m}$ below the surface, as shown in E; a plot showing vacancy distribution with depth as calculated by the Stopping Range In Matter (SRIM) code.

Analysis of the Raman spectroscopy data before irradiation (Figure 8) and after 0.2dpa of irradiation revealed the presence of a new Raman peak after irradiation. We believe this to be characteristic of the formation of new C-N bonds. This is the focus of continued investigation and will be combined with ongoing TEM imaging and diffraction analysis. We believe that this work is a key step to determining whether the presence of an additional thick BN substrate layer below the graphene may act to improve the radiation tolerance of the device when exposed to high energy irradiation (separating the graphene from charge build up in the underlying silica of the substrate).

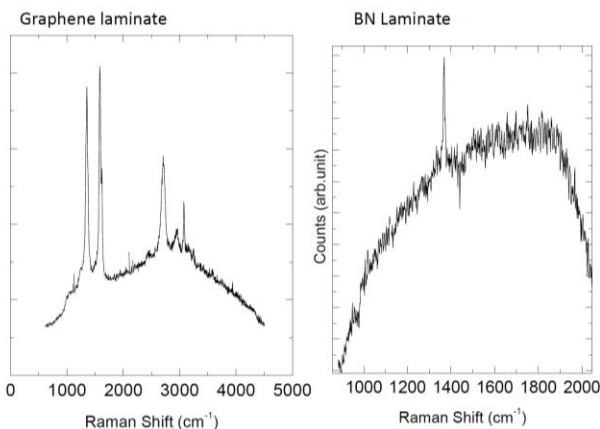


Figure 8: Raman Characterisation of graphene-BN laminate films before irradiation

4.5 Use of electron irradiation for controllable patterning of graphene BN heterostructures

Nano-patterned and suspended graphene membranes find applications in electronic devices, filtration and nano-pore DNA sequencing. However, the fabrication of suspended graphene structures with nanoscale features is challenging. We have investigated the direct patterning of suspended membranes consisting of a graphene layer on top of a thin layer of hexagonal boron nitride which acts as a mechanical support, using a highly focused electron beam to fabricate structures with extremely high spatial resolution within the scanning transmission electron microscope (STEM). The boron nitride support enables the fabrication of stable graphene geometries by preventing intrinsic strain in graphene membranes from distorting the patterned features. Line cuts with widths below 2 nm are reported (Figure 9 (I) and (II)). We also demonstrated that the extent of cutting can be monitored in situ utilising electron energy loss spectroscopy (EELS) by tracking of the carbon, boron and nitrogen K-edges.

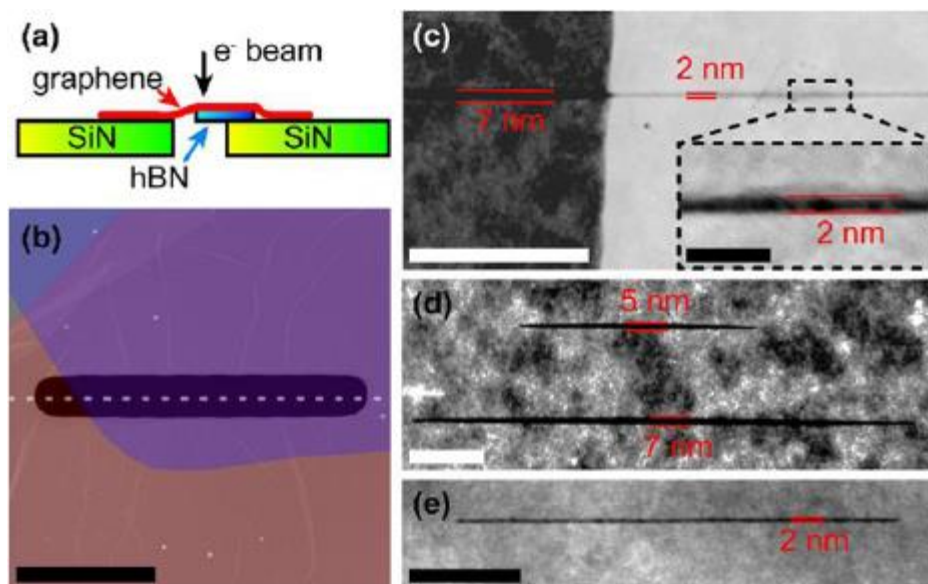


Figure 9 (I). Patterning suspended monolayer graphene and hBN supported monolayer graphene using a 1.4 nA STEM beam. (a) schematic showing the membrane structure when viewed in cross section at the position indicated by the dotted line superimposed on the image in (b). (b)–(e) HAADF STEM images illustrating the patterning of this structure. (b) Shows a low magnification image of the sample. The dark pill shape in the centre is the hole in the silicon nitride membrane. A 9 nm thick hBN flake covers the majority of the membrane and is false coloured blue. A monolayer graphene flake covers the entire membrane, and is false coloured red. Where the graphene is supported on the hBN is purple. The scale bar is 5 μm . (c) Shows a STEM cut from the suspended region of the graphene (left) to the supported region (right). The cut has a width of ~ 7 nm on the unsupported graphene, and a width of just ~ 2 nm on the hBN supported area. The linear electron fluence for this cut was 625 mC m^{-1} . The scale bar is 100 nm. The inset shows a higher magnification image of the indicated area. Small bridges over the cut are visible. The scale bar is 20 nm. (d) Shows 2 cuts in unsupported monolayer graphene with lengths of 161 and 332 nm, using equivalent linear fluences of 311 and 151 mC m^{-1} for the short and long cuts respectively. The cut features are broadened by tension within the membrane, with the widest areas in the centre of the cut. The scale bar is 50 nm. (e) Shows a long cut on a hBN supported region of monolayer graphene, with a linear fluence of 1.8 mC m^{-1} . In contrast to (d) no bowing or deformation of the membrane after patterning is visible. The scale bar is 50 nm.

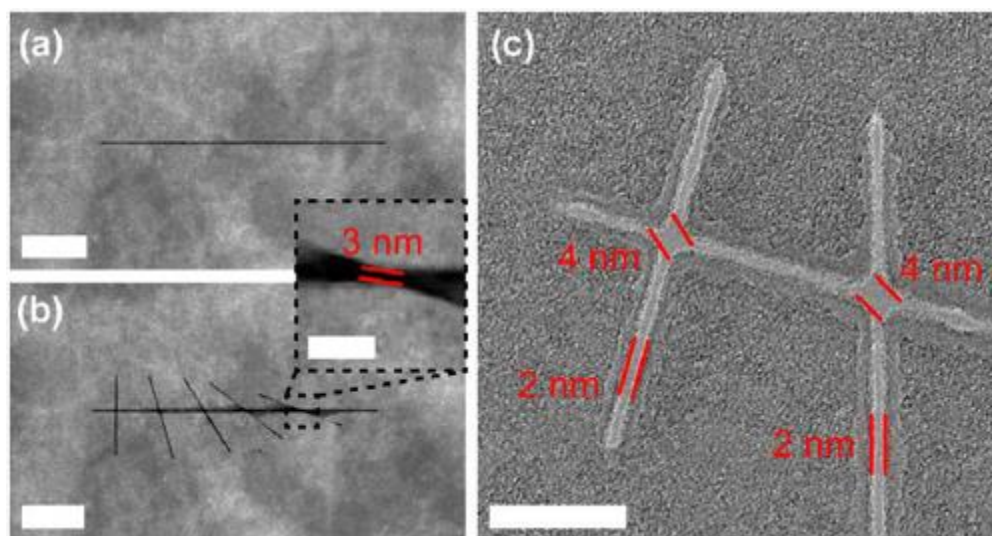


Figure 9(II). Patterning angled crosses in a graphene monolayer supported by 6.5 nm thick hBN. (a) Shows a HAADF image of initial line cut with a length of 220 nm, with an equivalent linear fluence of 1.64 mC m^{-1} . The scale bar represents 50 nm. (b) Shows a HAADF image of the location after a series of cuts of length 60–70 nm (line fluence $1.7\text{--}2 \text{ mC m}^{-1}$) crossing the initial cut, at angles of 90° , 75° , 58° , 36° and 20° to the initial cut. The scale bar represents 50 nm. The inset shows a higher magnification image of the most acute cross, showing a less than 3 nm gap between the opposite areas. (c) Shows a high magnification HRTEM image of the produced pattern. The scale bar represents 20 nm.

5. Studying radiation tolerance of layered silicates:

An alternative and perhaps more practical approach to improving the radiation tolerance of graphene devices could be to replace the standard oxidised silica substrate with a layered silica (e.g. mica). These are more widely available than suitable BN substrates and are known for their extremely flat surface. However, they have not previously been investigated as substrates for radiation hard graphene devices. In order to apply such devices it is necessary to understand the radiation response of the layered silicate substrates themselves. We have demonstrated imaging of the atomic structure of layered silicates using the scotch tape method to facilitate preparation of few layer samples and thereby provide exceptionally high resolution TEM imaging and even exit wave restoration of such materials (Figure 10 (I) and 10(II), reported in W Bower, et al Mineralogical Magazine, 79, 2 (2015) 337).

We then applied electron microscopy to study the effect of ion irradiation on the layered silicate mineral biotite. Our biotite samples were known to contain radioactive inclusions which produce radiohaloes in the surrounding structure. Using SRIM calculations we were able to predict the position of maximum radiation damage from the centre of the halo and to section this so that the material in this region could be imaged using transmission electron microscopy (Figure 11). This approach has allowed us to produce the first lattice resolution TEM images of the ion irradiation induced changes in silicate minerals. We

observe that the irradiation induced diffusion can cause dramatic changes in the basal plane lattice spacings (Figure 11 and 12) published as William R Bower, et al American Mineralogist, 101 (2016) 105.

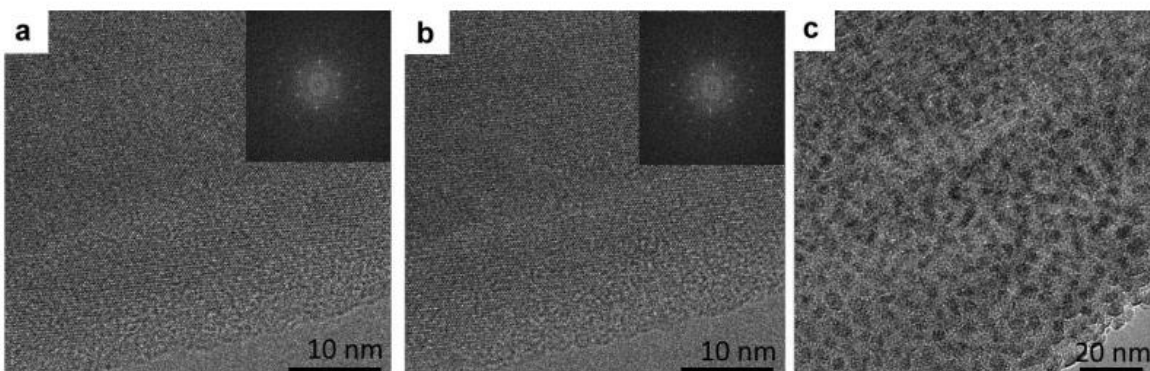


Figure 10 (I) : (a,b) High-resolution TEM images demonstrating the absence of electron beam-induced radiation damage up to a critical fluence. The Fourier transforms of the images (inset in a and b) show there was no loss of lattice information during image series acquisition. (c) The same area after >100 images: the mottled appearance demonstrates the presence of electron beam damage

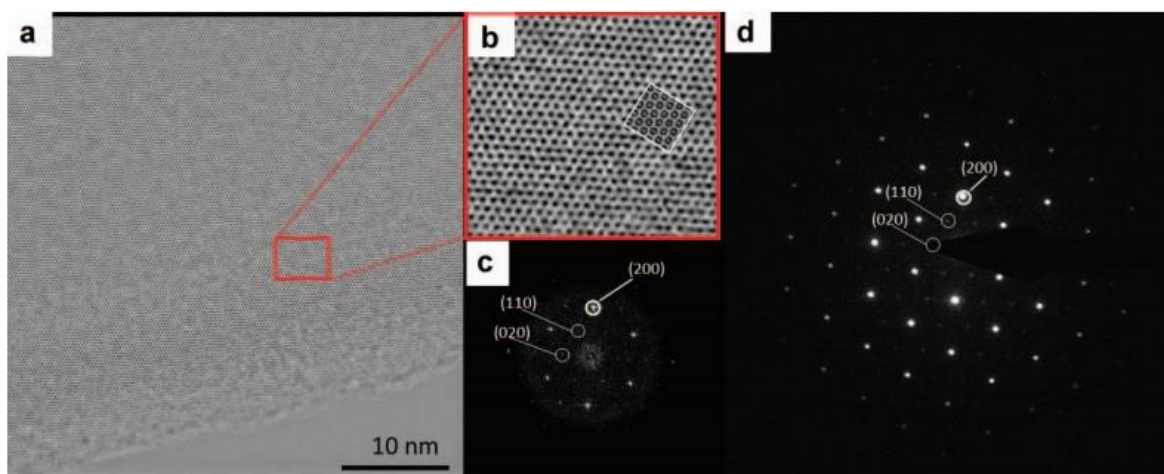


Figure 10 (II): (a) Phase of the exit wavefunction restored from a focal series of 20 high-resolution TEM images for biotite viewed along [001]. (b) An enlargement of the region shown by the red rectangle in (a) with the simulated phase of the exit wavefunction overlaid. (c) Fourier transform of the exit wavefunction revealing the presence of the weaker {110} and {020} lattice reflections in the restored exit wave which were not visible in the Fourier transform of a single high-resolution image due to the poorer signal-to-noise ratio (inset Fig. 4a). (d) Electron diffraction pattern from the same flake illustrating the presence of both the weaker reflections ({110}, {020}) and the stronger reflections such as {200}.

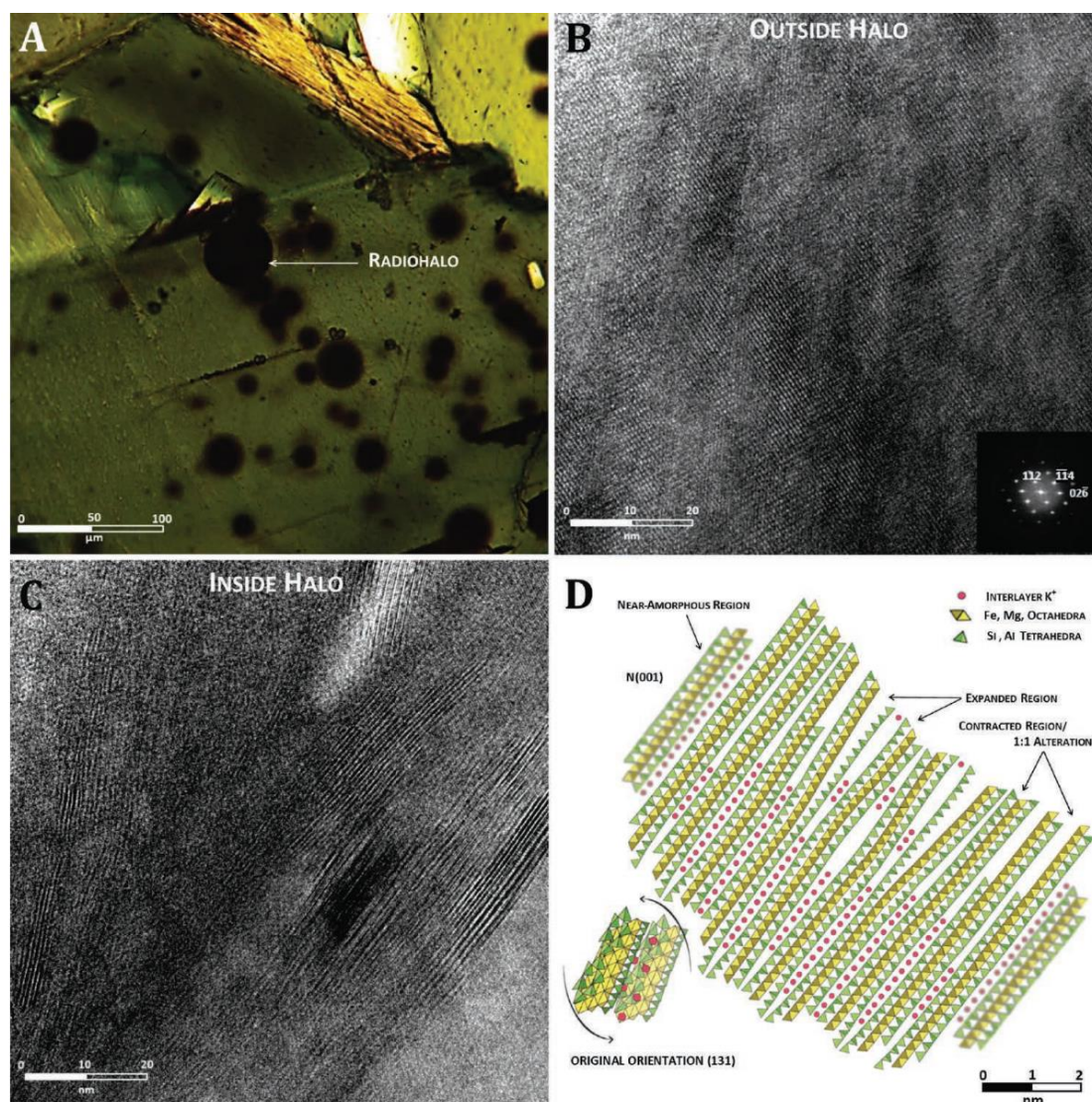


Figure 11: Demonstrating the effect of alpha ion irradiation on the structure of the layered silicate, biotite. (a) Optical microscope image of abundant, intensely darkened radiohaloes surrounding monazite (Th-rich) inclusions within biotite crystals. Discolored haloes result from radiation damage caused by α -particle bombardment over geologic timescales. Note that the differences in sizes of the haloes in this image stem from the different depths at which the haloes have been cross-sectioned. (b) HRTEM image of an area of unirradiated biotite crystal, outside of the halo area. Inset Fourier transform of this image demonstrates the periodicity of the biotite, oriented along $[131]$. (c) HRTEM image of an area of biotite inside the dark radiohalo, showing significant structural disturbance as a result of α -particle irradiation. Note the varied orientation of several discrete nanoscale regions including near-amorphous areas. (d) Schematic representation of the damaged crystal shown in c. Near-amorphous regions enclose neo-domains of radiation-damaged structure, displaying expansion and contraction of the silicate layers over nanometer-scale regions. Interlayer K^+ has likely been liberated or relocated across the crystal. Note the misorientation of the domains from the undamaged structure orientation $[131]$ to the damaged regions that are close to $[hk0]$.

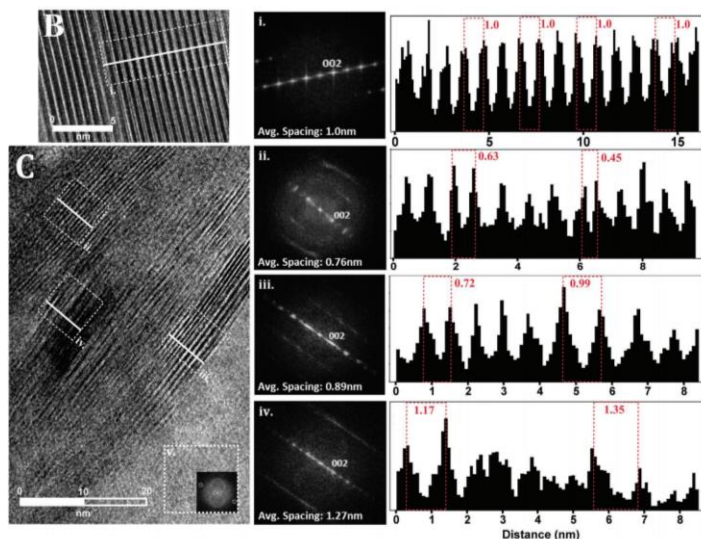


Figure 12: (b) TEM image taken from an undamaged crystal of biotite, viewed along the TOT layers. Note the prominent contrast of the phyllosilicate sheets. The average layer to layer spacing, measured from the adjacent Fourier transform of area i is 1 nm; consistent with the distance between the octahedral sheets in a model biotite crystal. (c) TEM image showing the damaged biotite structures found within the radiohalo, as shown in Figure 1c. Fourier transforms and intensity profiles for areas ii, iii, and iv illustrate the range of layer-to-layer spacings over the damaged regions. Area v shows a semi-amorphous bounding region; in which only two faint reflections are visible in the Fourier transform. From William R Bower, et al *American Mineralogist*, 101 (2016) 105.

Complementary experiments have investigated the irradiation damage of biotite minerals achieved by neutron irradiation of pristine biotite at the Dalton Cumbria Facility. We studied the structural changes in the irradiated materials using synchrotron microfocus X-ray diffraction and X-ray absorption spectroscopy. Biotite samples were prepared as thin (40 μm thick) cleavage parallel planes and mounted on glass slides for irradiation. As such, samples were irradiated along a plane normal to (001), perpendicular to the phyllosilicate layers. At doses up to 6.77 dpa in the region of highest particle fluence, biotite mica displays a heterogeneous structural response to irradiation on a micrometer scale, with sequential dilation and contraction of regions of the structure perpendicular to the sheets, as well as a general overall contraction of the phyllosilicate layer spacing. At the peak of ion fluence, the structure collapses under a high point defect density and amorphous areas are pervasive among altered domains of the original lattice. Radiation-induced reduction of structural iron at the region of highest structural damage across an α-particle's track has been demonstrated by Fe K-edge X-ray absorption near edge spectroscopy (XANES) and local structural disorder has been confirmed by analysis of both potassium K-edge XANES and Fe K-edge extended X-ray absorption fine structure analysis (Figure 13).

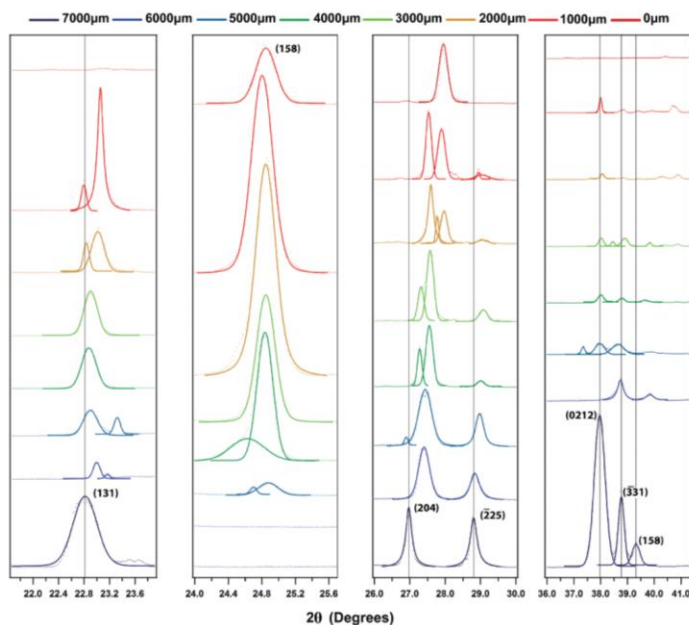


Figure 13: 1D X-ray diffraction patterns showing the changes in peak position and intensity as a function of ion beam dose (higher radiation dose was experienced at the centre of the ion beam irradiation designated as 0 μm and roughly equal to $\sim 6.8\text{dpa}$) and reduced at greater distances from the centre. Patterns were acquired every 5 μm but are displayed here only at 1000 μm intervals. The sample received a total dose of $9.2 \times 10^{15} \text{ } ^4\text{He}^{2+}$ ions (5 MeV) across the beam profile, published as William R. Bower, Carolyn I. Pearce, Andrew D. Smith, Simon M. Pimblott, J. Frederick W. Mosselmans, Sarah J. Haigh, James P. McKinley, Richard A.D. Patrick, *American Mineralogist*, 101, 4 (2016), 928

Our improved understanding of the structural radiation damage response of silicate minerals provides a solid basis towards application of these materials as substrate for radiation hard graphene devices.

6. Irradiation damage in novel 2D materials beyond graphene.

Many layered materials can be cleaved down to individual atomic planes, similar to graphene, but only a minority of these materials are stable under ambient conditions. The rest react and decompose in air, which has severely hindered their investigation and potential applications towards improved electronics and sensors to combat WMD. Other work has successfully demonstrated the types of radiation induced defects that can be formed in MoS₂ and WS₂ using the transmission electron microscope but little is known about irradiation induced changes for 2D materials that are unstable in air. We have been working in collaboration with Dr Gorbachev in the National Graphene Institute to demonstrate a new remedial approach based on cleavage, transfer, alignment, and encapsulation of air-sensitive crystals, all inside a controlled inert argon atmosphere. This approach has allowed us to study two archetypal two-dimensional crystals that are of intense scientific interest but are unstable in air: black phosphorus (BP) and niobium diselenide. These materials are produced in the glove box inert atmosphere and built into a device where they are encapsulated by graphene or BN, which protect them from environmental degradation (Figure 14)

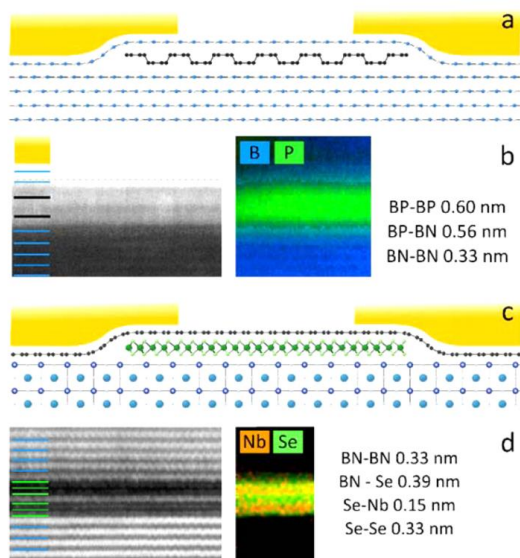


Figure 14. Glovebox encapsulated air-sensitive 2D crystals. (a) Schematics of the studied BP devices: mono- or few-layer BP is placed on an hBN substrate and protected with hBN. (b) Left: Cross sectional high-angle annular dark-field STEM image of a heterostructure consisting of bulk hBN/bilayer BP/bilayer hBN and a top gold contact. Interlayer distances found from such images are stated on the right. Center: STEM image superimposed with elemental profiles for the boron-K edge (blue) and phosphorus-L2,3 edge (green) that are found using EEL spectrum imaging for the same area. (c) Schematics of our NbSe₂ devices: 2D NbSe₂ is placed on hBN or atomically flat STO and covered with monolayer graphene. (d) Left: Cross-sectional bright field STEM image of a bulk hBN/bilayer NbSe₂/bulk hBN with the extracted interlayer distances on the right. Center: Superimposed STEM-EEL spectrum image with elemental profiles for the niobium-M4,5 edge (orange) and selenium-L3 edge (green). Reproduced from our paper Cao, et al Nano letters 15 (8), 4914-4921 (2015).

6.1 Superconductivity and irradiation induced defects in monolayer NbSe₂

Bulk NbSe₂ consists of covalently bonded Se–Nb–Se layers assembled in A-B-A-B fashion by weak (vdW-like) Se–Se bonding. It is a type-II s-wave superconductor with the transition temperature, T_C , of 7.2 K. However, recent work has found that thin NbSe₂ crystals deteriorate greatly, disallowing devices thinner than several nanometers. The latter observation agrees with our own efforts to study superconductivity in 2D NbSe₂ using the standard microfabrication procedures that work well for graphene and air stable dichalcogenides. The disagreement between different studies can be attributed to either accidental polymer contamination that coated and protected NbSe₂ or the use of lithographic techniques, which enhance oxidation during UV exposure. Our field-effect devices made from NbSe₂ monolayers are conductive and fully stable under ambient conditions, which is in contrast to the counterparts processed in air. NbSe₂ remains superconducting down to the monolayer thickness and is the first mechanically exfoliated monolayer material to exhibit superconductivity (Figure 15).

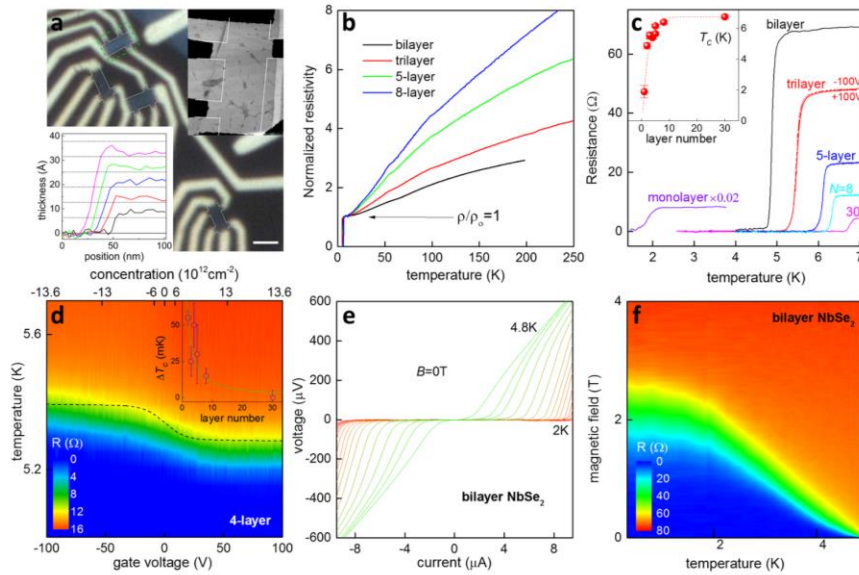


Figure 15. Electron transport and superconductivity in few-layer NbSe₂. (a) Optical micrograph showing four multiterminal NbSe₂ devices encapsulated with graphene. Scale bar: 2 μm. Left bottom inset: AFM measurements of thickness for several encapsulated NbSe₂ samples. Right top inset: AFM topography for one of the devices (outlined with the green box in the main image) before its etching to define the Hall bar mesa (its later position is indicated by the white lines). (b) Resistance as a function of T for representative devices with different N . Resistivity is normalized to its value near the superconducting transition. (c) Changes in T_C with N . The dotted line in the inset is a guide to the eye. (d) Example of maps $R(V_g, T)$ measured near the superconducting transition for $N = 4$. The black dashed curve shows its expected shift. The upper x-axis is nonlinear and corresponds to the field-induced Δn . Inset: Changes in the critical temperature ΔT_C for different N , which correspond to sweeping V_g between 0 and +100 V. The green curve shows the expected functional dependence $\Delta T_C \propto 1/N$. (e) Voltage–current characteristics at different T for bilayer NbSe₂. (f) Superconducting phase diagram $R(B, T)$ for the same device. All the presented data are for NbSe₂ on STO and devices encapsulated with monolayer graphene. Reproduced from our paper Cao, et al Nano letters 15 (8), 4914-4921 (2015).

Studies of irradiation damage in NbSe₂ have demonstrated for the first time the structure of atomic defects within monolayer NbSe₂ encapsulated in graphene (Figure 16, published as Nguyen et al ACS Nano, 2017, 11 (3), pp 2894–2904). By combining atomic resolution TEM imaging, density functional theory (DFT) calculations, and strain mapping using geometric phase analysis we demonstrated the presence of stable Nb and Se monovacancies in monolayer material and reveal that Se monovacancies are the most frequently observed defects, consistent with DFT calculations of their formation energy (Figure 17 (I)). We studied the evolution of different types of point defect over time (Figure 17 (II)) and found that the number of point defects was stable for a fixed imaging dose, suggesting that radiation damage has a critical flux below which little further damage is introduced.

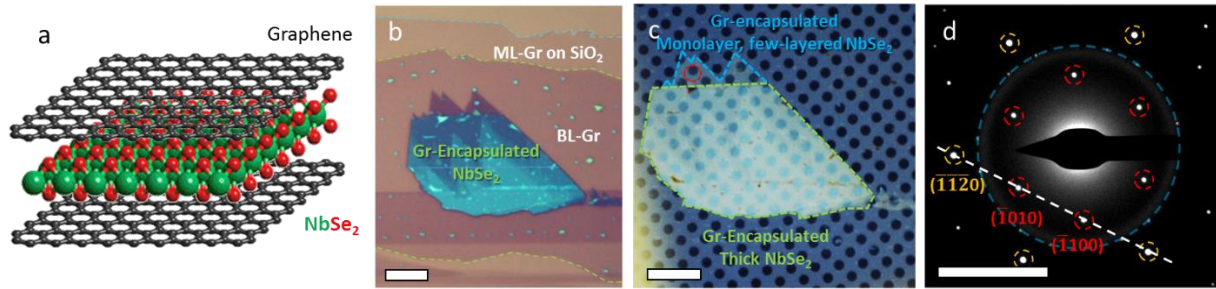


Figure 16: Imaging of graphene-encapsulated monolayer NbSe₂ made by mechanical exfoliation in argon-environment glovebox. (a) Schematic of graphene encapsulated NbSe₂ stack. (b) Optical image showing NbSe₂ flake encapsulated between graphene sheets on oxidised silicon wafer. Thin regions were identified by optical contrast. (c) Same flake transferred to a quantifoil TEM grid. Blue dashed outline shows thin and monolayer regions at the edge of the flake which are examined with atomic-resolution TEM (scale bar: 10 μ m). (d) SAED pattern from red ring in (c), the blue dashed ring highlights reflections from the encapsulating graphene sheets (10 $\bar{1}$ 0), $d=0.213\text{nm}$; red circles highlight NbSe₂ (10-10), reflections ($d=0.296\text{nm}$); while orange circles highlight NbSe₂, (11-2 0), $d=0.173\text{nm}$ Line profile shows relative intensities of (10-1 0) and (11-2 0) diffraction spots used to determine specimen thickness (scale bar: 5 nm^{-1}). Reproduced from our paper Nguyen et al ACS Nano, 2017, 11 (3), pp 2894–2904

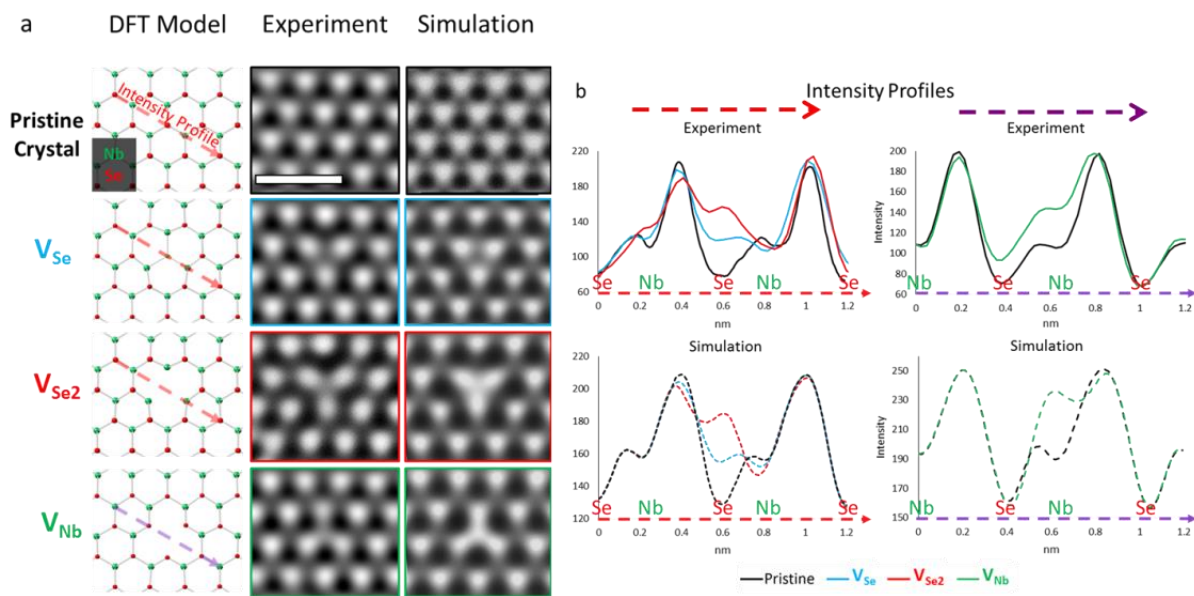


Figure 17(l). Experimental and simulated images for vacancy point defects in monolayer NbSe₂. (a) DFT relaxed structural models (left), high resolution TEM images (center), and multislice calculations (right) for pristine material (black border), a Se monovacancy (V_{Se}, blue border), a Se divacancy (V_{Se2}, red border), and a Nb vacancy (V_{Nb}, green border) (scale bar: 1 nm). (b) Intensity profiles extracted along the armchair direction as shown by arrows in (a) for experiment (upper panels) and simulation (lower panels) demonstrating the ability to distinguish pristine crystal from V_{Se}, V_{Se2} (left) and V_{Nb} vacancies (right) using their individual intensity signatures. Reproduced from our paper Nguyen et al ACS Nano, 2017, 11 (3), 2894–2904.

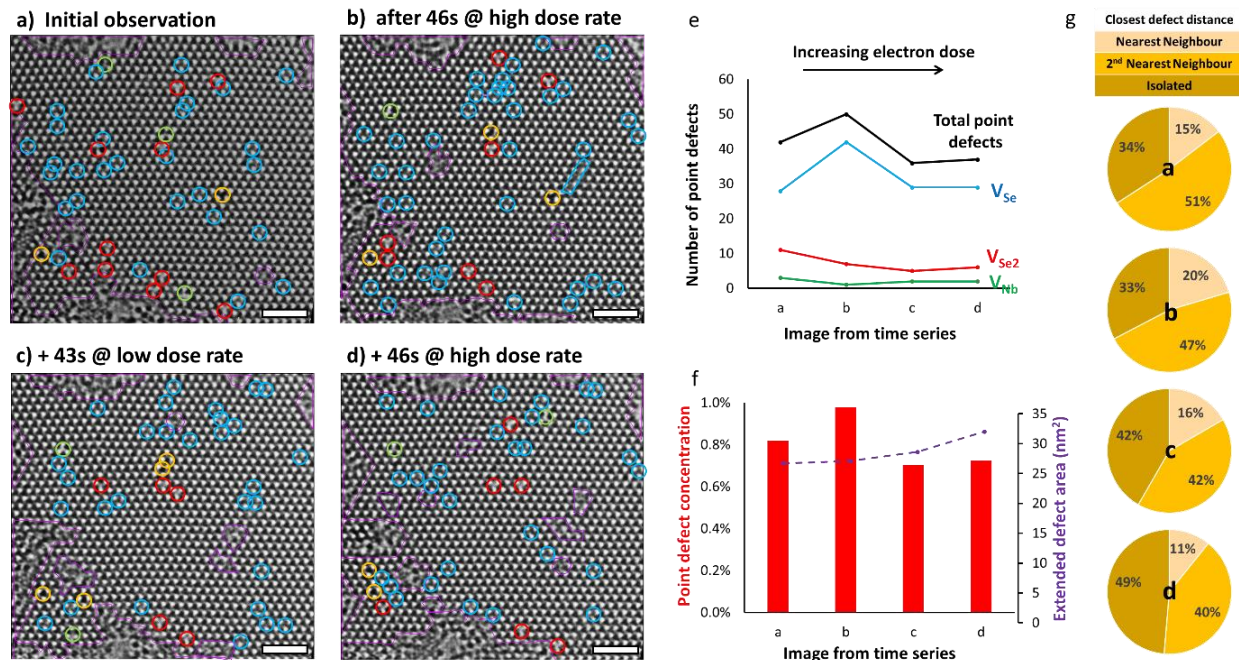


Figure 17(II). Point defect populations in NbSe₂ with continuous electron irradiation. Atomic resolution TEM imaging of monolayer NbSe₂ (a) on first observation and (b) after continuous imaging with a high dose rate: $1.4 \times 10^6 \text{ e} \cdot \text{\AA}^{-2} \text{ s}^{-1}$ for 46 s (total dose: $6.5 \times 10^7 \text{ e} \cdot \text{\AA}^{-2}$). Immediately after acquiring (b) the beam was spread to reduce the electron dose rate to $\sim 1 \times 10^3 \text{ e} \cdot \text{\AA}^{-2} \text{ s}^{-1}$. (c) The same area after 43 s of low dose rate imaging (total accumulated dose of $6.5 \times 10^7 \text{ e} \cdot \text{\AA}^{-2}$) and (d) the same area after another 46 s of high dose rate imaging (total accumulated dose of $1.3 \times 10^8 \text{ e} \cdot \text{\AA}^{-2}$). Colored rings indicate the nature of point defects: blue, Se monovacancy, V_{Se} ; red, Se divacancy, V_{Se2} ; green, Nb monovacancy, V_{Nb} ; and yellow, Pt atom. Purple borders indicate larger, agglomerated regions of defects. Scale bars: 2 nm. (e) Summary of the total number of point defects and the total area taken up by larger defect regions in the images (a)–(d). (f) Plot of the percentage of point defects observed in (a)–(d). (g) Clustering analysis considering the distance between each point defect and its nearest neighbor defect. Any defects separated from their nearest neighbors by more than two nearest neighbor distances are considered to be “not clustered” (isolated). Reproduced from our paper Nguyen et al ACS Nano, 2017, 11 (3), 2894–2904.

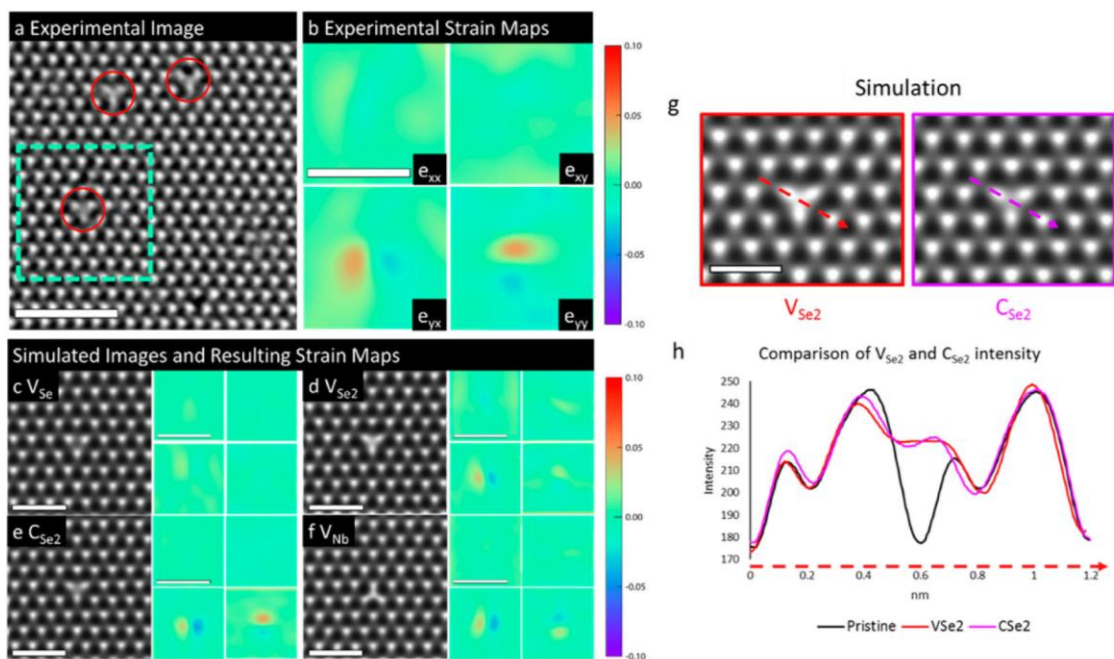


Figure 18. Geometric phase analysis (GPA) allows identification of impurity substitution into Se divacancy defects. (a) TEM image of a region containing three divacancy-type defects (circled red) and (b) corresponding strain component maps for the representative defect within the green box in (a). In e_{yx} and e_{yy} regions of tension and compression are observed horizontally and vertically across the defect (scale bars: 2 nm). (c–f) GPA strain analysis from TEM image simulations for (c) a Se monovacancy, V_{Se} ; (d) a Se divacancy, V_{Se2} ; (e) a carbon-substituted Se divacancy, C_{Se2} ; and (f) a Nb monovacancy, V_{Nb} . The experimentally observed strain around the defect very closely matches the simulations for a C_{Se2} . (g) TEM image simulations comparing V_{Se2} and C_{Se2} . (h) Intensity profiles from the lines indicated in (g) reveal that TEM image contrast alone cannot be used to distinguish between these two types of defects (scale bars are 1 nm for multislice images and 2 nm for GPA maps). Reproduced from our paper Nguyen et al ACS Nano, 2017, 11 (3), pp 2894–2904

We further studied that in the presence of adventitious impurities of C, N, and O, these can substitute into the $NbSe_2$ lattice stabilizing Se divacancies (Figure 18). We also observe evidence of Pt substitution into both Se and Nb vacancy sites. This knowledge of the character and relative frequency of different atomic defects provides the potential to better understand and control the unusual electronic and magnetic properties of this exciting two-dimensional material.

6.2 Transport properties of irradiated few layer black phosphorus

Black phosphorus, BP, has attracted huge interest during the last few years. Its atomic layers have a hexagonal structure, similar to graphene, but strongly corrugated. The changes in symmetry make BP a semiconductor with a direct band gap that strongly depends on the number of layers. As it is made progressively thinner, the direct band gap in BP varies from ~ 0.3 eV in bulk to ~ 1.5 eV for a monolayer. Crystals only a few nanometers thick demonstrate high carrier mobility (reported hole mobility of 5200

$\text{cm}^2 \text{V}^{-1} \text{s}$ at room temperature and $45000 \text{ cm}^2 \text{V}^{-1} \text{s}$ below 20 K(15)) and high on–off ratios in field-effect devices (up to 10^5) offering potential for applications in high-speed optoelectronic devices.

Black phosphorus is thus a complementary addition to the 2D materials library, providing a variable band gap between those of graphene (no band gap) and semiconducting 2D-dichalcogenides (which lie between 1.3 and 2 eV). Nonetheless, the exploitation of BP's electronic properties is hampered by the material's strong susceptibility to oxidation in the presence of air. This degradation is amplified by humidity, exposure to light and elevated temperatures leading to a drastic deterioration of BP's electronic and optical properties. The observed degradation rate increases for thinner BP flakes, with monolayers visibly degrading over the course of a few minutes and even relatively thick (10 nm) crystals degrading to form droplet-like oxidation bubbles within 24 h in air. The etching process in thicker flakes (>50 nm) is observed to self-terminate after a few days due to the accumulation of oxidized phosphorus (PxOy) forming a protective layer on the surface of the flake.

We studied mono- and bi- layer crystals of BP by atomic force microscopy (AFM) and optical spectroscopy. Starting with a trilayer, our glove box fabricated phosphorene devices reach sufficiently high mobilities to exhibit Landau quantization, unlike conventionally produced black phosphorus materials (Figure 19, published as Cao, et al Nano letters, (15), 8 (2015), 4914).

We have also investigated the effect of irradiation for tuning the electronic transport properties of BP encapsulated between graphene or boron nitride sheets (Figure 20). By investigation of different flux and fluence regimes, we observe that above a critical irradiation fluence, electron beam irradiation causes damage to the protective graphene or BN sheets, allowing oxidative species from the environment to degrade the encapsulated BP (Figure 20). We observe that the etching process is self limiting – a stable phosphate species is formed around the damaged area which protects other areas of the crystal. This provides a mechanism to lithographically pattern BP with improved resolution compared to traditional etching regimes.

To demonstrate local etching of BP we exposed a set of 100 nm long lines into a graphene encapsulated 3 layer BP crystal using a focused STEM probe, as shown in Figure 20. By progressively increasing the electron dose used to make the cuts (pixel dwell-times varied between (i) 0.05 and (vi) 2.5 s with 100 pixels and 1.3 nA beam current, 200 kV) we change the amount of damage induced which becomes clearly visible at the dose of (iv) $\sim 3 \times 10^9 \text{ e nm}^{-1}$ as a clear-cut approximately 3 nm wide through the entire BP film thickness. Further increase in dose leads to effective broadening of the cut up to 5 nm at $2 \times 10^{10} \text{ e nm}^{-1}$. We then exposed the sample to air and ambient light for 2 days and repeated the imaging to find that the cuts have expanded laterally and had identical contrast for all exposure doses above 10^9 e nm^{-1} . The resulting line width was found to be 6–10 nm wider than before air contact giving the smallest feature size of 9 nm (for the 0.25s dwell time), (Figure 20(II)).

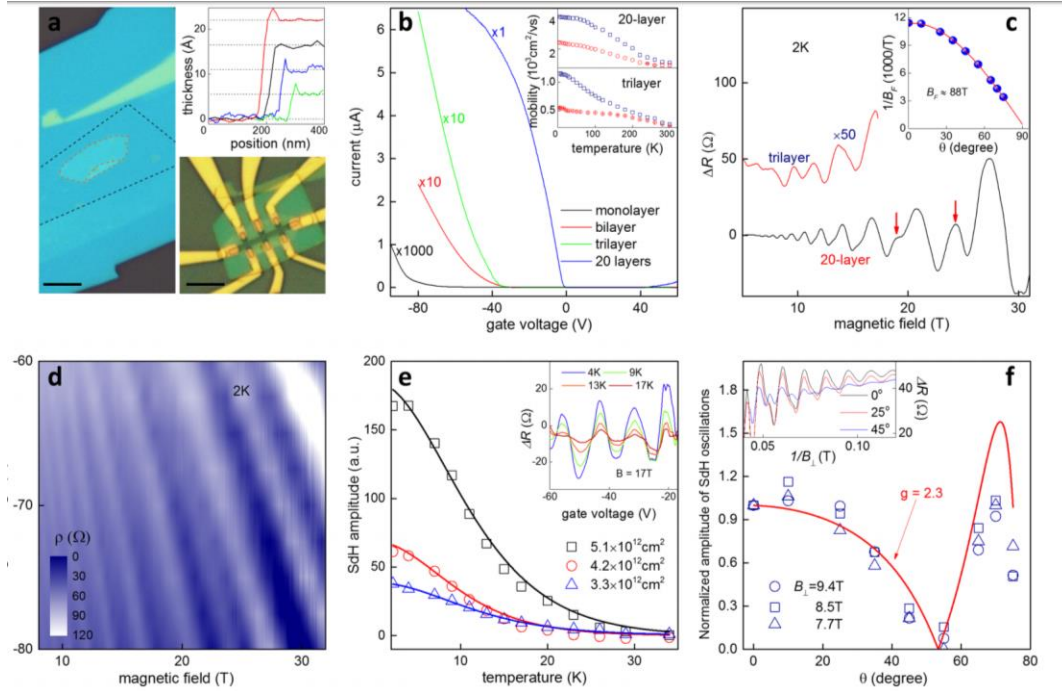


Figure 19: Transport properties of atomically thin BP. (a) Left: Trilayer BP crystal (outlined in red and partially folded) is encapsulated with monolayer hBN outlined with the black lines. Right top – AFM measurements of thickness for several encapsulated BP samples. The dashed lines correspond to the BP interlayer spacing of 5.5 Å. Right bottom: Optical micrograph of one of our typical Hall bar devices. Scale bars: 5 μm . (b) Source-drain current at 10 K as a function of V_g for BP devices of different thickness, bias voltage 30 mV. Inset: T dependences of μ found using Hall and field-effect measurements (red and blue curves, respectively) for 3- and 20-layer BP. (c) Changes in resistance (ΔR) for the devices in (b). The red arrows mark spin-splitting of Landau levels. Inset: Angle dependence of the oscillation frequency. (d) Color map $\rho(V_g, B)$ for the 20-layer device, Ohms. (e) T dependence of SdH oscillations. Inset: Examples at different temperatures. Their amplitude can be fitted by the Lifshitz–Kosevich formula (solid curves in the main plot). (f) Amplitude of SdH oscillations in the 20-layer BP for different orientations of magnetic field. Examples are shown in the inset. Reproduced from our paper Cao, et al Nano letters 15 (8), 4914-4921 (2015)

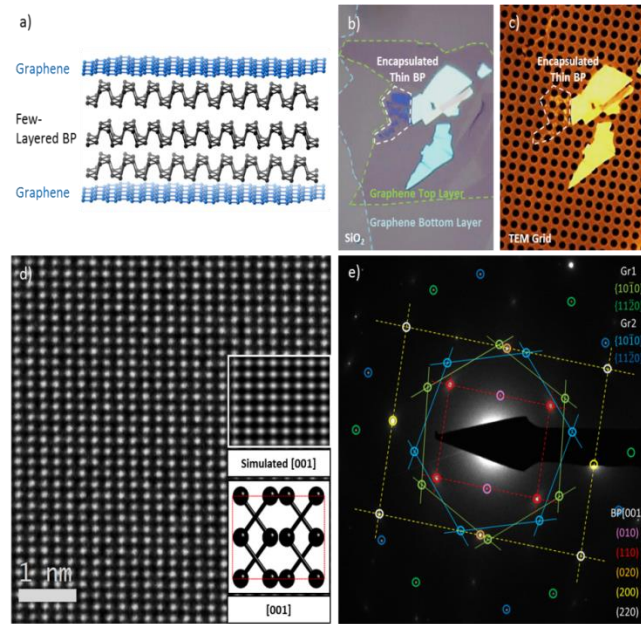


Figure 20 (I): a) Schematic of the graphene-encapsulated BP sample. b) Optical micrograph of such a heterostructure on an oxidized silicon wafer, dashed lines highlight edges of mechanically exfoliated crystals. All exfoliation and transfer is performed in an argon environment glove box to prevent oxidation during the sample fabrication. c) The same sample transferred to a Quantifoil TEM grid. d) Atomic-resolution Wiener-filtered aberration-corrected TEM image of pristine BP flake, with image simulation and ball-and-stick inset showing the [001] orientation. e) Diffraction pattern from the encapsulated 5 layer thick BP crystal, showing spots for upper and lower graphene sheets (misoriented by $\sim 20^\circ$) and BP (010), (110), (020), (200) and (220) diffraction spots. The red box in the centre connecting (010) and (110) diffraction spots highlights forbidden reflections which are only visible in few-layered BP flakes. Reproduced from Clark et al Nano Letters, 2018, 18 (9), pp 5373–5381.

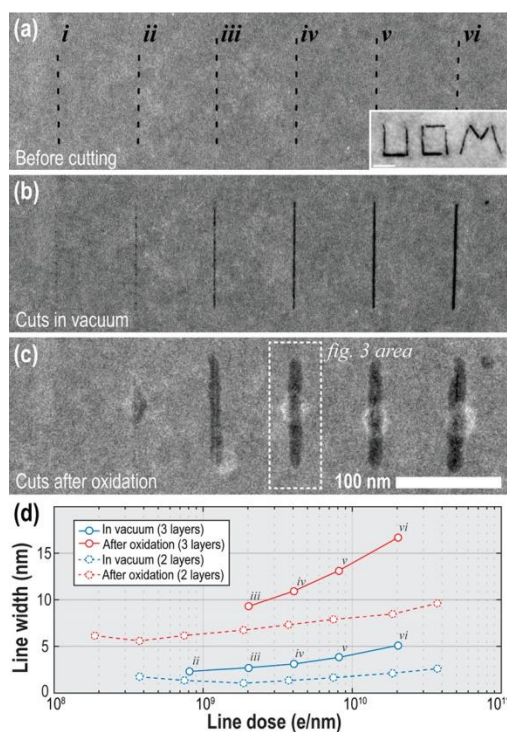


Figure 20 (II). HAADF STEM images showing the controlled cutting of nm-resolution lines in an encapsulated (3 layer) BP flake. The width of the 100 nm long cuts is controlled by varying dwell time per pixel (i) 0.05, (ii) 0.1, (iii) 0.25, (iv) 0.5, (v) 1, and (vi) 2.5 s. Lines were drawn using a probe current of 1.3 nA, an accelerating voltage of 200 kV and 1 pixel/nm. (a) shows the area immediately prior to patterning. (b) Cuts immediately after patterning. (c) Same cuts after exposing sample to air at room temperature for 2 days. (d) Solid lines are a comparison of line widths on initial sculpting in the electron microscope (blue data) and after oxidation in air (red data) taken from the area shown in parts a–c. The dashed lines show the change in line widths in a 2 layer sample as pictured in supporting material Figure S10. The inset in part a is a demonstration of electron beam writing of “UOM” into a 10 nm thick BP crystal (scale bar: 20 nm). Reproduced from Clark et al Nano Letters, 2018, 18 (9), pp 5373–5381.

By performing non-negative matrix factorization (NMF), the EEL spectra in the region of the phosphorus L edge was blindly separated into components corresponding to BP signals (L2,3 onset around 132 eV, L1 peak around 188 eV) and oxidized phosphorus, or PxOy (L2,3 onset around 137 eV, L1 peak around 193 eV). The BP and PxOy characteristic spectra, and the maps of their strength, are shown in Figure 21. The PxOy signal is clearly maximized around the edges of the cut region, suggesting that a passivating barrier has indeed been formed. Mapping of the carbon K edge indicates that the graphene sheets have not been affected by the oxidation process, while oxygen K-edge mapping suggests an increased level of elemental oxygen in the etched region, although the signal-to-noise ratio is too low to observe increased levels around the edge, as suggested by the PxOy map.

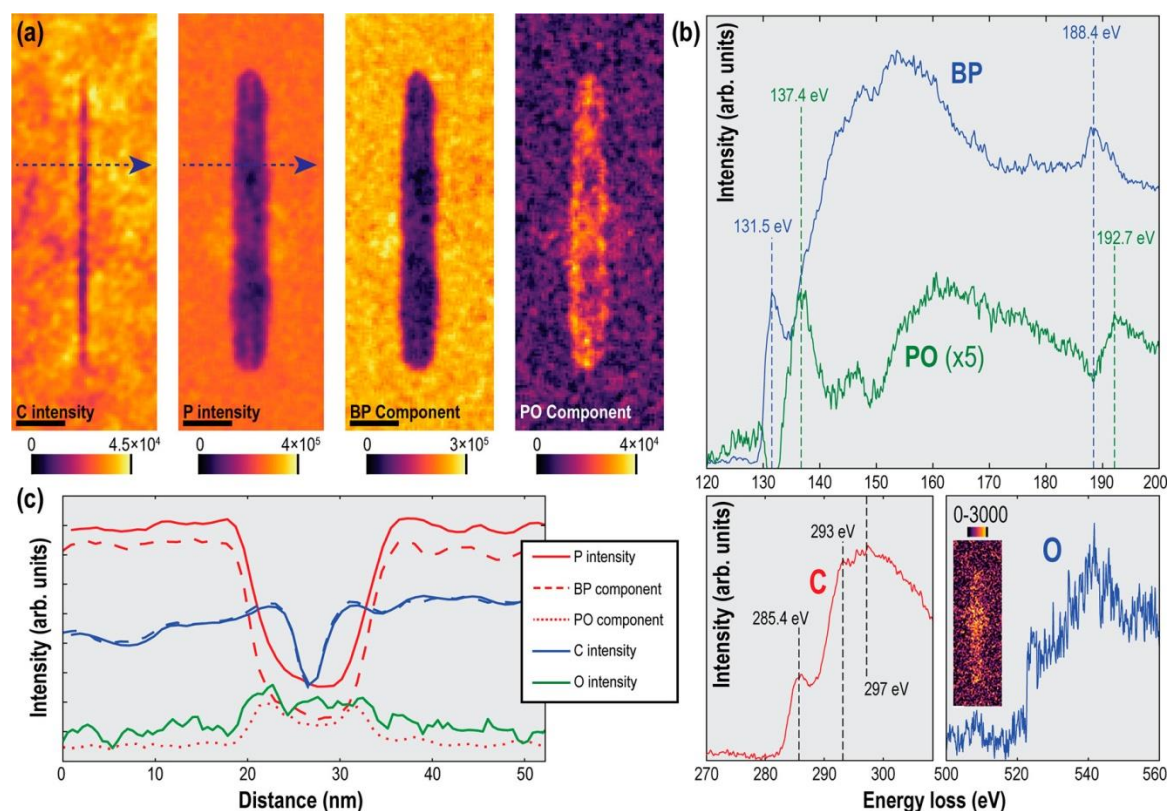


Figure 21. EEL spectrum imaging of the cut feature labeled (iv) in Figure 19c after oxidation. (a) Shows maps of the absolute intensity of the carbon K edge and the phosphorus L edges obtained by model based least-squares fitting of the spectra at every pixel, along with maps of the components of the phosphorus L edges extracted using NMF algorithm corresponding to BP and oxidized phosphorus (PxOy). Scale bars are 20 nm. (b) NMF factors corresponding to the BP and PO signals around the phosphorus L edges, as well as extracted carbon and oxygen K edges. The inset on the O K-edge plot is a map of the absolute intensity of the oxygen edge. (c) Relative elemental intensities (shown by solid lines) along the profile indicated by the dotted line in part a. The dotted lines representing the separated BP and PO components are scaled by fitting their combined intensities to the elemental P intensity. Reproduced from Clark et al Nano Letters, 2018, 18 (9), pp 5373–5381.

To test the electrical transport properties of our patterned structures, we have produced and selectively oxidized two hBN encapsulated BP devices, with BP thicknesses of 2 and 4 layers respectively as measured using the atomic force microscope (AFM). The lower encapsulating hBN layer had a thickness of ~ 20 nm, and the upper hBN layer was a monolayer. After encapsulation the sample was transferred to a silicon wafer coated with a 300 nm thick thermal oxide layer, to enable electrical gating of the BP. Gold was then deposited to create high quality electrical contacts as described in our previous glovebox work.

Prior to the selective oxidation process, both devices demonstrated classical field effect behavior with hole mobilities of $2000 \text{ cm}^2/(\text{V s})$ and $200 \text{ cm}^2/(\text{V s})$ for 4L and 2L respectively, similar to earlier reports on encapsulated BP devices. We then used a 100 kV electron beam lithography instrument (Raith EBPG 5200) to expose narrow lines across the conductive channel as indicated by the red lines in Figure 22a,b. After the sample was exposed to ambient conditions, this exposure effectively separated contacts 2 and 3 from the rest of the device with a low bias resistivity higher than 108Ω , well above the 103Ω value measured before the etching procedure (Figure 22c). The realistic etched line width is estimated to be 12 nm taking into account the 4 nm pattern size exposed with a 2–3 nm beam diameter and including the 6 nm oxidation broadening. It is surprising that a gap only 12 nm wide spanning across $1 \mu\text{m}$ sample size shows such a high resistivity at room temperature (reproducible in both 2L and 4L devices). Furthermore, no leakage current was observed while increasing the bias voltage up to 100 mV giving breakdown field of at least 107 V/m, better than that of vacuum. While the etched regions of the sample changed their conductivity dramatically, other unexposed areas (all other contacts) showed very little change, ruling out the possibility of accidental device degradation between the measurements.

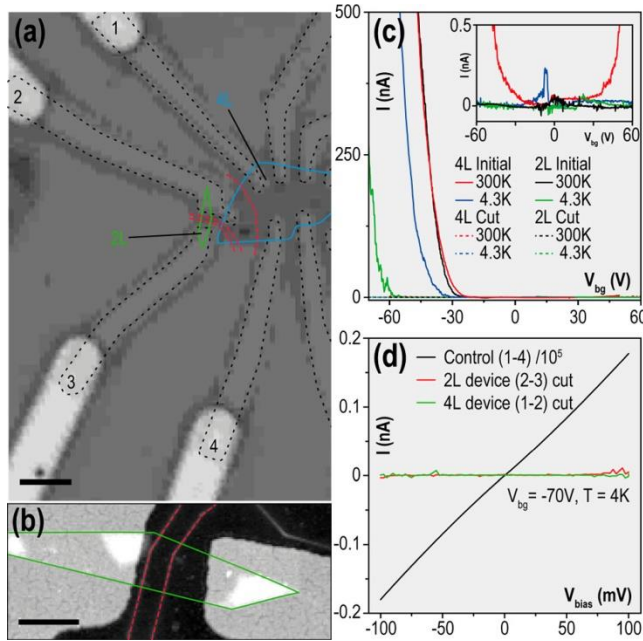


Figure 22. Electrical characterization of patterned few layer BP. (a) Optical micrograph of a BN encapsulated BP device with multiple metallic contacts highlighted by black dashed line. Blue line shows edges of 4 layer BP flake (4L) and green line 2 layer BP flake (2L). Red lines indicate etched lines (b) AFM topography of the 2L device with crystal edges highlighted with green. (c) Electrical current measured in a two terminal configuration (between contacts 1–2 for the 4L flake and 2–3 for the 2L flake) before and after the etching procedure. The inset shows the dotted traces (voltages after patterning) with a reduced vertical scale to enhance visibility. (d) Current voltage characteristics measured across the 2L and 4L devices compared to unetched 4L sample (contacts 1–4). Scale bars: (a) $2 \mu\text{m}$ and (b) 500 nm . Reproduced from Clark et al Nano Letters, 2018, 18 (9), pp 5373–5381.

6.3 Exfoliating natural minerals to produce new 2D crystals for radiation sensors?

Franckeite is only one of a wide variety of natural mineral phases in which van der Waals layers are stacked together with imperfect lattice matching such that the repeat period along one of more direction extends to a pseudo-unit cell several nanometers in length. Our results have demonstrated that such systems may provide a possible route to a new family of 2D systems.

Our work has demonstrated exfoliation and isolation of 2D flakes from the natural mineral Franckeite. These have been tested and revealed exceptionally promising electrochemical properties so have application in energy storage. Electrical devices have been fabricated and shown p-type electrical conductivity. Furthermore the material can be liquid exfoliated via sonication in common solvents eg. NMP. (Figure 23, published as M Velický et al, Nature Communications 2017 shows structural characterization where the layerd structure of these materials is revealed. The material consists of alternating cubic PbSbS and hexagonal SnFeS layers with a periodicity along [010] of ~3 nm.

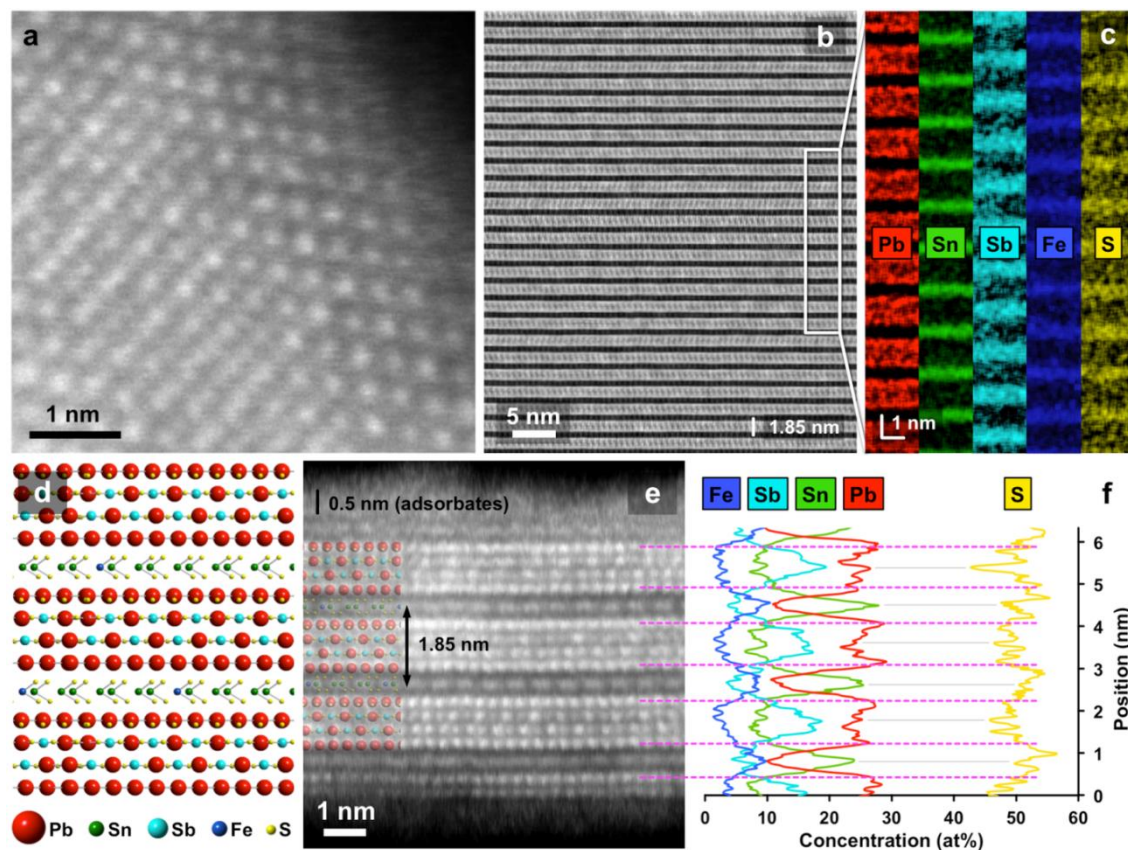


Figure 23: Revealing the atomic structure of the 2D crystal Franckeite. (a) High angle annular dark field scanning transmission electron microscope (HAADF STEM) plan view image of flake, (b) Cross sectional view of thick flake with elemental analysis from energy dispersive X-ray spectroscopy (c). (d) Atomic schematic, (e) HAADF STEM image in cross section for a 3 layer exfoliated flake, (f) Elemental analysis of different layers. Reproduced from our paper M Velický et al, Nature Communications, 2017.

Irradiation testing of Franckeite and more recently another misfit layer compound (cylindrite) is a focus of a current work in the final stages of preparation. Initial tests show highly unusual irradiation behavior with the PbS layer extending into the hexagonal SnS type phases (Figure 24, unpublished). This is expected to have a dramatic effect on optical and electrical properties so could provide a sensitive radiation sensor. This is the focus of ongoing work.

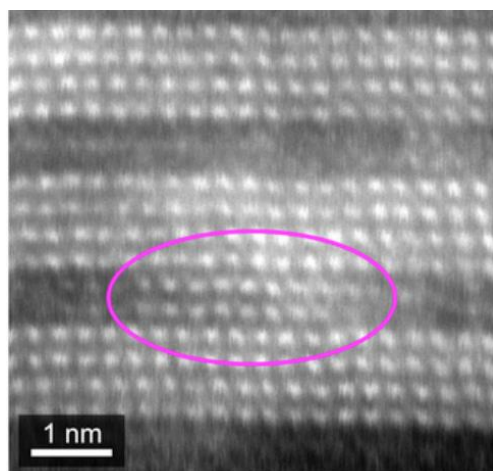


Figure 24: Franckeite atomic structure after electron irradiation. Purple oval highlights where cubic PbS has formed in the previously hexagonal SnFeS layers. Paper in preparation.

6.4 Irradiation induced defects in monochalcogenides

GaSe and InSe are important members of a new class of 2D materials, the III-VI metal monochalcogenides, which are attracting considerable attention due to their promising electronic and optoelectronic properties. We have investigated point and extended atomic defects formed in mono-, bi-, and few-layer GaSe and InSe crystals. Using state-of-the-art scanning transmission electron microscopy (STEM), it is observed that these materials can form both metal and selenium vacancies under the action of the electron beam (Figure 25 and 26). Selenium vacancies are observed to be healable; recovering the perfect lattice structure in the presence of selenium or enabling incorporation of dopant atoms in the presence of impurities. Under prolonged imaging, multiple point defects are observed to coalesce to form extended defect structures, with GaSe generally developing trigonal defects and InSe primarily forming line defects (Figure 27). These insights into atomic behavior could be harnessed to synthesize and tune the properties of 2D post transition metal monochalcogenide materials for optoelectronic applications (published as Hopkinson et al ACS Nano, in press 2019).

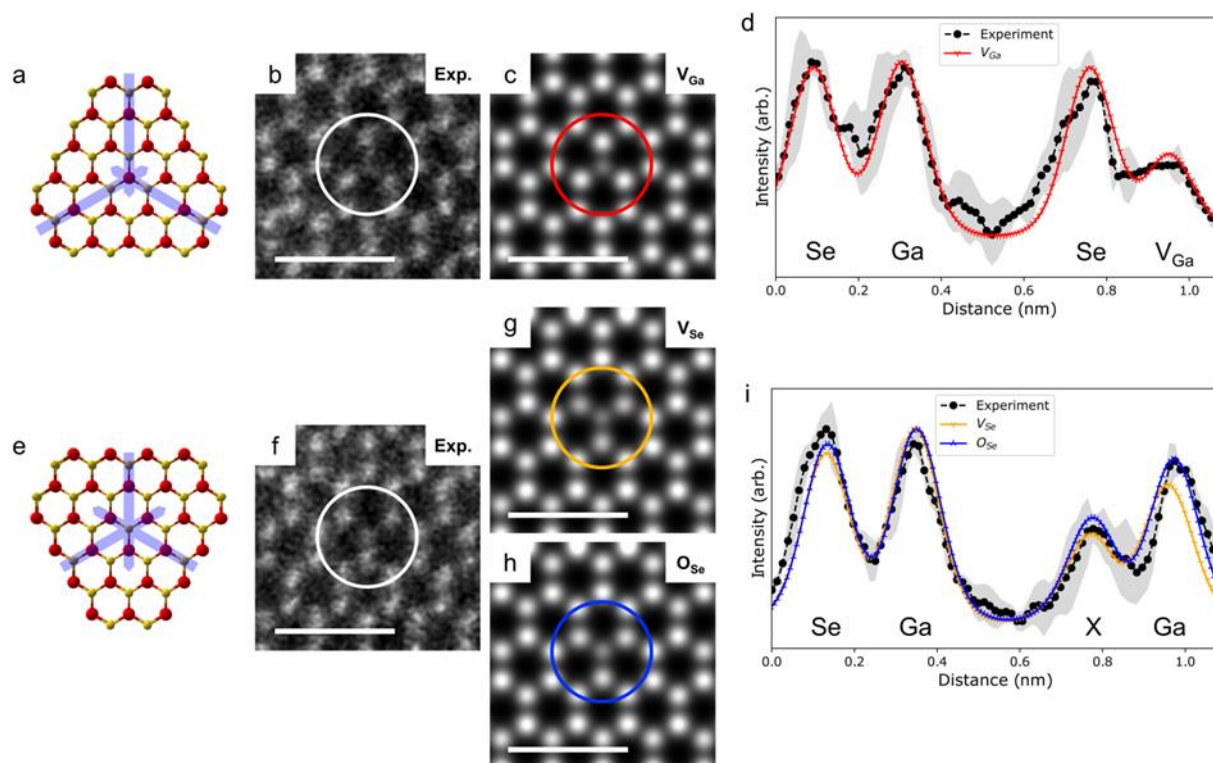


Figure 25 – Identification of point defects in monolayer GaSe. (a, e) Atomic models of monolayer GaSe with corresponding line profile directions indicated for gallium and selenium site defects. (b, f) Experimental images of a point defect at a gallium site and at a selenium site, respectively. (c, g, h) Simulated ADF images of a gallium monovacancy, VGa, a selenium monovacancy, VSe, and an oxygen substitution, OSe. All scale bars: 1 nm. (d, i) Comparison of normalized experimental and simulated ADF intensity across the defects in (c, g, h). Experimental profiles were averaged for the symmetrically equivalent [110], [1-20], and [-210] armchair directions (indicated by the blue lines in a and e), with the grey shading indicating one standard deviation error. The position of the defect site on the line scan is indicated by VGa or X. Reproduced from our paper Hopkinson et al ACS Nano, in press 2019.

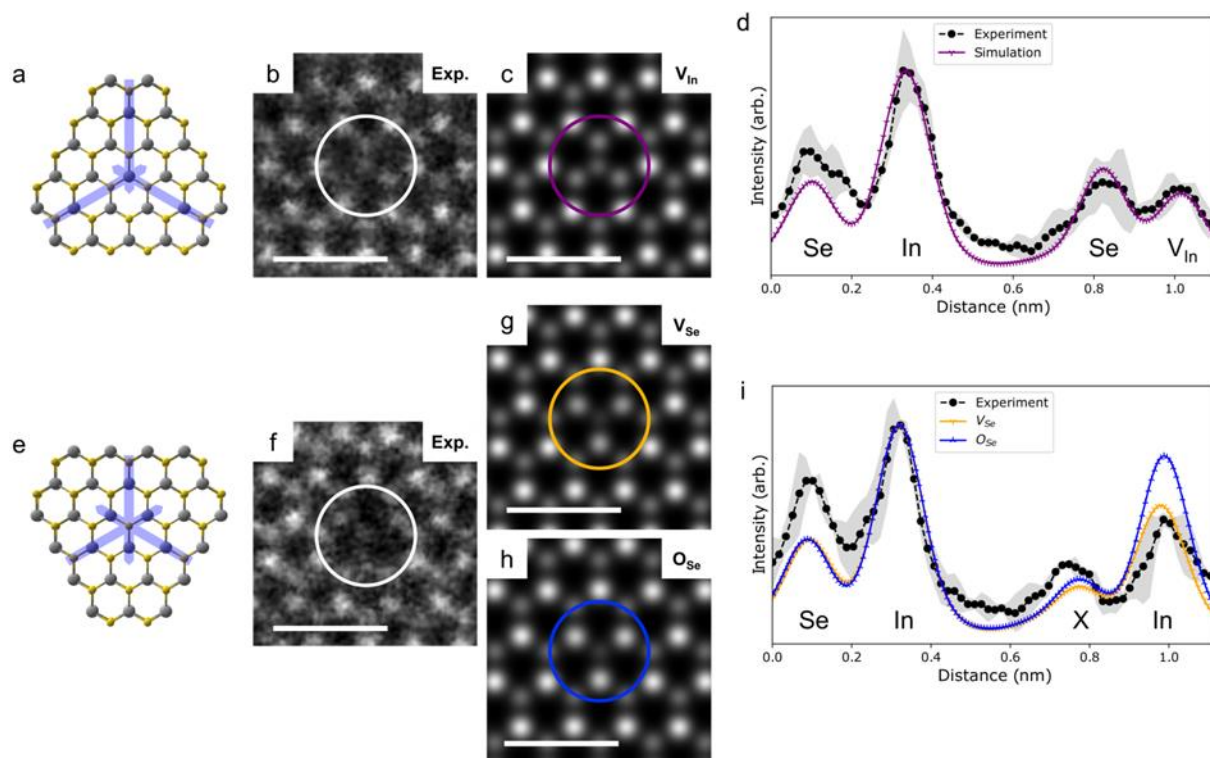


Figure 26 – Identification of point defects in monolayer InSe. (a, e) Atomic models of monolayer InSe, with line profile directions indicated for indium and selenium site defects. (b, f) Experimental images of a point defect at an indium site and a selenium site respectively. (c, g, h) Simulated ADF images of an indium monovacancy, V_{In} , a selenium monovacancy, V_{Se} , and an oxygen substitution, O_{Se} . All scale bars: 1 nm. (d, i) Comparison of normalized experimental and simulated ADF intensity across the defects in (c, g, and h). Experimental profiles were averaged for the symmetrically equivalent $[110]$, $[1-20]$, and $[-210]$ armchair directions (indicated by the blue lines in a and e) with the grey shading indicating one standard deviation error. The position of the defect site on the line scan is indicated by V_{In} or X. Reproduced from our paper Hopkinson et al ACS Nano, in press 2019.

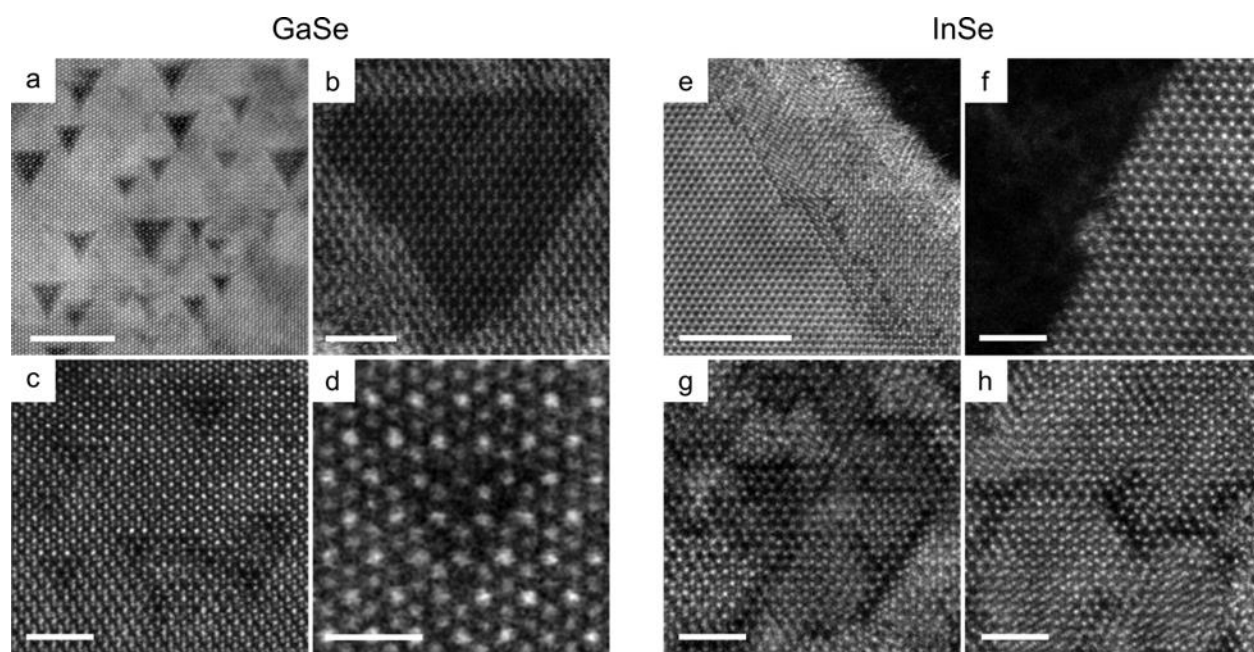


Figure 27 – Comparison of extended defects in GaSe and InSe. (a) Time averaged ADF image of clustered, stable trigonal defects in thick (>10 layer) GaSe after a cumulative fluence of $\sim 8 \times 10^6 \text{ e}^{-\text{\AA}^{-2}}$. Scale bar: 5 nm. (b) Trigonal defect in bilayer AA-stacked GaSe exposing a monolayer region of crystal. Scale bar: 2 nm. (c) Clustered trigonal defects in bilayer ϵ -GaSe. This was the first image captured of this area of crystal, with a cumulative fluence of $\sim 1.3 \times 10^5 \text{ e}^{-\text{\AA}^{-2}}$. Scale bar: 2 nm. (d) Detail of trigonal defect shown top right in (c). Scale bar: 1 nm. (e) Atomically sharp step edge neighboring a semi-crystalline crack edge in few-layer InSe. Scale bar: 5 nm. (f) Atomically sharp, reconstructed edge in monolayer InSe. Scale bar: 2 nm. (g, h) Selenium vacancy zigzag line defects in bilayer γ -InSe. Scale bar: 2 nm. Reproduced from our paper Hopkinson et al ACS Nano, in press 2019.

7. Professional development

This grant and the exciting work resulting from it has been a major contributor to the exceptionally fast academic progression of the PI, springboarding her from newly appointed lecturer in 2011 to full professor in 2018. She has given over 60 invited presentations, including ones at the most prestigious microscopy meetings (European Microscopy Congress, etc) and plenary opening/closing presentations. She was awarded a 1.3M euro Starting Grant from the European Union to extend the work begun in option years 1 and 2. She was awarded the Royal Microscopy Society Award for Innovation in Physical Sciences, and the UK Institute of Materials Minerals and Mining's Premier Award, the Rosenhain Medal. The project has also contributed to the PI being awarded over £12M in additional PI or Co-PI grant funding from the UK research councils, many of which are directly contributing to improving our understanding of the irradiation damage in novel materials with defense applications.

The success of this work has greatly contributed to allowing Co-PI, Prof Donnelly to obtain >£3.5M investment from the UK government to upgrade the in situ TEM irradiation facility. This new state of the art instrument came online in 2018 and is already contributing to furthering of our understanding of ion irradiation in a wide range of materials. <https://research.hud.ac.uk/institutes-centres/centres/ibc/facilitiesandequipment/miami-2/> One of the world's foremost irradiation damage facilities ; the MIAMI microscope allows simultaneous ion irradiation and electron microscopy imaging of a wider range of ion species with higher energy and greater resolving power than was previously possible. The work funded by DTRA was key to demonstrating the need for greater resolving power, leading to the instrument upgrade.

Prof Andre Geim is one of the world's most highly cited researchers and continues to publish regularly in Science and Nature. Prof Irina Grigorieva and been promoted to full Professor and is leading the highly successful doctoral training programme, graduating over 100 students with expertise in 2D nanomaterials (including Dr Aidan Rooney, mentioned below). This grant initiated and cemented the highly productive collaboration between Prof Geim, Prof Grigorieva and Prof Haigh to allow irradiation damage studies to be performed on the latest generation of emerging 2D materials in the most timely manner possible.

The postgraduate research student, now postdoctoral researcher, Dr Aidan Rooney, has completed his PhD research after completing the taught part of the NowNANO PhD programme in May 2012. He has developed a wide range of skills with focused ion beam sample preparation, transmission electron microscope imaging and in-situ ion irradiation though visits to Prof Donnelly's research group in Huddersfield. He has presented posters at various student run conferences in England, presented posters at DTRA 2014, M&M 2014, EMC 2016 and IWEPM 2016, and gave an oral presentation at MCC 2015. He successfully obtained an independent fellowship funding (1 year) under the EPSRC's doctoral First fellowship scheme. He has now moved to a prestigious postdoctoral role with Dr Cooper at a national laboratory in France. The postgraduate student Lan Nguyen published several high impact papers and successfully graduated in 2018. He has now moved to a permanent job for Oxford City Council. Doctoral student, Dr Alex Rakowski, graduated in 2018 and received commendation for his thesis. He recently obtained a fantastic postdoctoral position at Penn State in the USA and is continuing to collaborate to write up the work he completed during his PhD. Masters student, Mr Sean Lawlor, worked on NbSe₂ data processing and successfully graduated with an MPhil in 2018, going on to complete a PhD at Cardiff University. Dr Eric Prestat has been successful in obtaining a full academic lecturer post at the University of Manchester (from Jan 2017).

The volume and quality of the research published as part of this grant has contributed to Manchester's growing reputation as a centre of excellence for 2D materials discovery. Exemplified by the UK government's decisions to host the Royce Centre for Advanced materials at Manchester (<https://www.royce.ac.uk/> opening 2019), the £61M National Graphene Institute (<https://www.graphene.manchester.ac.uk/about/ngi/> (opened in 2016 co-funded with the European Union) and the £60M Graphene Engineering and Innovation Centre (<https://www.graphene.manchester.ac.uk/about/geic/> (opened in 2018, focused on the rapid development and scale up of graphene and other 2D materials applications).

8. Public Dissemination Activities

The results of this work have contributed to a wide range of graphene-based outreach activities, with all student's, researchers, PIs and Co-Is participating in these efforts.

During this grant Prof Sarah Haigh and Prof Andre Geim have made several appearances on national TV and radio promoting graphene science. For example, in April 2013 they both appeared in the BBC Horizon Innovation program discussing the graphene's potential in high mobility electronics. Our work relating to TEM imaging of graphene at Manchester has also been featured on the BBC one show and BBC News. Sarah Haigh has also recently appeared on the BBC 2 documentary "Inside the factory" discussing the potential applications of graphite beyond pencils.

The PI, Dr Sarah Haigh, is actively involved in the University of Manchester's regular outreach activities aimed at promoting the importance of graphene for future applications. She has visited schools and given talks/demonstration at University open days. She is an elected member of the Worshipful Company of Armourers and Brasiers Material Science committee which contributes ~£300k annually to support Science Outreach projects. Her Armourers Ambassadors challenge continues to create new resources to help explain Material Science to secondary school pupils and has recently scaled up production of such resources to create 100 activity kits which will be available for schools to borrow free of charge.

Dr Aidan Rooney has contributed significantly to a wide range of different events (e.g. 'Meet the Nanoscientists at the Museum of Science and Industry, The Big Bang Science Fair 2016)) and through these activities has completed his STEM Ambassador Outreach Training. Aidan attended 'Commercialisation of research' course (January 2014 - June 2014) and his group were the winners of £10k funding in the 'Venture Further' Enterprise Graphene competition 2014. Aidan also participated in the National "3 minute Thesis Competition and was the Manchester Finalist, He participated in the National 1 minute thesis competition and won the "People's choice Award". Aidan also successfully applied and was awarded the opportunity to present our research in the "STEM for Britain" meeting in the Houses of Parliament (Westminster, London) where student's present their work to the UK Members of Parliament.

Mr Alex Rakowski regularly demonstrated Manchester's unique imaging capabilities to groups of school pupils visiting the department (~9 times per year from 2015-2018). Dr Lan Nguyen, Mr Sean Lawlor, Dr Sarah Haigh, Prof Andre Geim and Prof Irina Grigorieva have participated in the production of an art photography book "A random walk through Graphene" published in November 2016.