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# Imaging Two Dimensional Materials and their Heterostructures

R Zan<sup>1</sup>, Q M Ramasse<sup>2</sup>, R Jalil<sup>3</sup>, J-S Tu<sup>4</sup>, U Bangert<sup>5</sup> and K S Novoselov<sup>4</sup>

<sup>1</sup>Department of Physics, Omer Halisdemir University, Nigde, Turkey

<sup>2</sup>SuperSTEM, STFC Daresbury Laboratory, Warrington, UK

<sup>3</sup>Department of Physics, University of Engineering & Technology, Lahore, Pakistan

<sup>4</sup>School of Physics and Astronomy, The University of Manchester, Manchester, UK

<sup>5</sup>Department of Physics and Energy, University of Limerick, Ireland

recep.zan@ohu.edu.tr

**Abstract.** Stacking different two-dimensional (2D) atomic layers is a feasible approach to create unique multilayered van der Waals heterostructures with desired properties. 2D materials, graphene, hexagonal boron nitride (h-BN), molybdenum disulphate (MoS<sub>2</sub>) and graphene based van der Waals heterostructures, such as h-BN/graphene and MoS<sub>2</sub>/graphene have been investigated by means of Scanning Transmission Electron Microscopy (STEM).

## 1. Introduction

In recent years, two-dimensional (2D) materials including graphene, hexagonal boron nitride (h-BN), and transition metal dichalcogenides (TMDs) have attracted great attention for applications in fields. In particular, the combination of these layered materials to obtain van der Waals heterostructures is of remarkable interest [1].

Single layer hexagonal boron nitride (h-BN) in contrast to a gapless semiconductor graphene has a wide band gap of ~5.9 eV, which arguably makes it the thinnest possible insulator and therefore a perfect candidate for incorporation into heterostructures [2]. One of the most studied heterostructure type is known to be graphene/h-BN. More recently, transition-metal dichalcogenides such as molybdenum disulphide (MoS<sub>2</sub>) and tungsten disulphide (WS<sub>2</sub>) have also been under heavy investigation as a new class of materials with remarkable properties. By implementing these single layer materials into graphene based devices, the device performance can be enhanced [3]. Single layer MoS<sub>2</sub> is a direct gap semiconductor with 1.8 eV that is different from its bulk form and it has an indirect band gap of 1.2 eV [4]. Although electrical, magnetic and mechanical studies of 2D materials and their combination to obtain heterostructures are established, there is a lack of direct atomic visualisation of these systems, thus limiting our understanding of these highly exciting materials [5,6].

In this paper, we present a (S)TEM study of graphene/h-BN and graphene/MoS<sub>2</sub> heterostructures with an emphasis on their lateral interfaces where heterostructures meet the graphene layer.



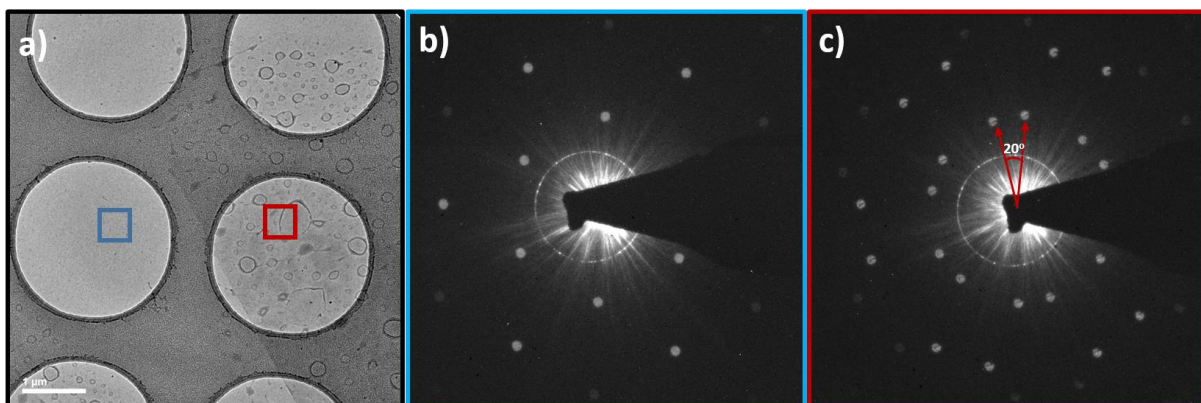
## 2. Experimental

Graphene, h-BN and MoS<sub>2</sub> were prepared via mechanical exfoliation technique from their bulk. Graphene, h-BN and MoS<sub>2</sub> layer numbers were identified via light microscopy and Raman spectroscopy. Following the fabrication and characterization of the 2D materials, h-BN layer was transferred onto graphene layer via wet chemistry approach to obtain graphene/h-BN heterostructure by using mask aligner. The same procedure was implemented to fabricate graphene/MoS<sub>2</sub> heterostructure.

Screening and diffraction imaging of the samples were carried out in a stationary transmission electron microscopy mode (TEM) in a FEI Tecnai F30. The detailed electron microscopy studies were performed in an aberration corrected dedicated STEM (Daresbury SuperSTEM) at low primary beam energy (60 kV) with angstrom-sized probe. This acceleration voltage is known to be lower than the threshold of knock-on damage for most of the sensitive 2D materials. Atomic sites of carbon, boron, nitrogen, molybdenum and sulphur atoms and lateral interface of the heterostructures were directly revealed in medium angle annular dark field (MAADF) imaging and high angle annular dark field (HAADF) imaging mode by their approximate  $Z^2$  dependence and electron energy loss spectroscopy (EELS). All presented images in this paper are raw (unprocessed).

## 3. Results and Discussion

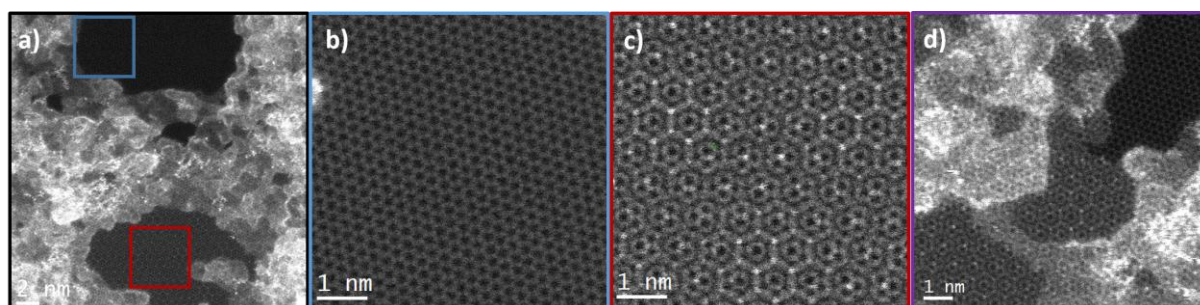
Figure 1 shows low magnification TEM image and diffraction patterns of the graphene/h-BN heterostructure. In the low magnification TEM image in figure1(a) four holes in lacey carbon film on the TEM grid are fully covered with single layer graphene and the single layer h-BN covers almost two holes, the right side of the figure1(a). As a result of this, we managed to investigate the junction between graphene and the heterostructure. As can be seen in the same figure, h-BN covering the region of graphene (heterostructure) can reveal itself with bubbles, darker and thicker regions due to the transfer of h-BN onto graphene as the transfer process involves chemicals that are expected to contaminate the structure. The transfer process may also lead to strain in the heterostructure. The diffraction patterns of the graphene layers and the heterostructure that were taken from the colored boxes in figure1(a) are presented in figure1(b) and figure1(c) respectively. The diffraction pattern of graphene confirms that the graphene is purely single layer as shown in figure1(b). Since graphene (2.46 Å) and h-BN (2.52 Å) have similar lattice constants, they both appear very similar in the diffraction pattern as shown in figure1(c). There are 12 spots in the inner (and outer) set of spot, 6 of which belong to graphene and the other 6 to h-BN layer.



**Figure 1.** Low magnification TEM and diffraction images of the graphene/h-BN heterostructure, taken at 300kV.

It is found that the angle between the closest spots which are graphene and h-BN spots is measured to be about  $20^\circ$ . This angle also represents the rotation between the layers with respect to each other. As a result, the overlapping graphene and h-BN layer to create heterostructure can cause Moire patterns which have larger periodicities than graphene and h-BN depending on the rotation angle of the layers. Moire pattern is observed even in perfect matching due to the 1.8% difference in the lattice constant between graphene and h-BN [7,8].

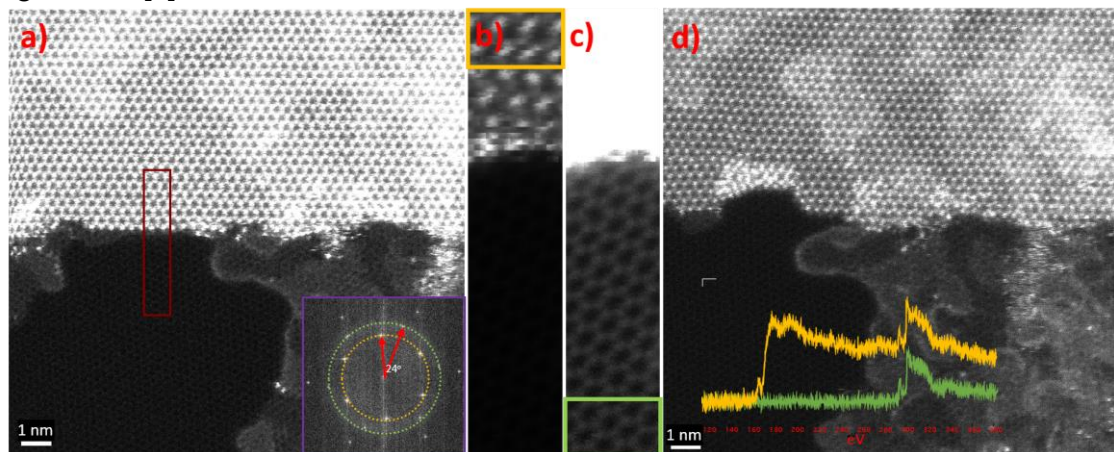
Figure 2 shows STEM-MAADF images of the graphene/h-BN heterostructure as taken at 60kV acceleration voltage. The heterostructure and graphene junction is shown in figure2(a). However, the lateral interface is not clearly visible due to the hydrocarbon contamination over the junction. However, the graphene side of the junction can be seen in figure2(b) as a magnified image of the blue box in figure2(a). Similarly, a closer look at the red box in figure2(a) shows graphene/h-BN heterostructure that reveals itself via Moire pattern that has different periodicity than graphene or h-BN (figure2c). In order to avoid contamination over the junction and to be able to observe the lateral interface, beam shower (about 10mins) was applied to the region that was to be imaged. As a result of this, as can be seen in figure2(d), a clear transition from graphene to heterostructure was observed. However, while imaging the region, we observed knock on damage after few minutes of beam scanning on the h-BN layer at the interface. This is due to the weak bonding at the edge compared to the basal plane as damaging wasn't noticed in the basal plane. On the other hand, much faster damaging of h-BN compared to graphene/h-BN heterostructure was observed in our previous experiments (only h-BN imaging) [9]. Therefore, we can conclude that graphene serves as a shield for h-BN against radiation damage. Additionally, graphene damaging was not encountered during the experiments, either.



**Figure 2.** STEM-MAADF images of the graphene/h-BN heterostructure, taken at 60kV.

Similar to graphene/h-BN heterostructure, graphene/MoS<sub>2</sub> heterostructure was prepared by transferring single layer MoS<sub>2</sub> onto single layer graphene. STEM-HAADF images of graphene/MoS<sub>2</sub> heterostructure are illustrated in figure 3. A STEM-HAADF image of the heterostructure and graphene junction is shown in figure3(a) where the dark region represents graphene and the bright side is the heterostructure. Due to the large difference between atomic numbers of graphene ( $Z_C=6$ ) and MoS<sub>2</sub> ( $Z_{Mo}=42$  and  $Z_{S}=2 \times 16$ ), the contribution of the graphene to the atomic contrast in the HAADF images (approximate  $Z^2$  dependence) is minimal and this effect is clearly visible in figure3(a). The FFT of the heterostructure that is presented as inset figure3(a) shows the angle between graphene and MoS<sub>2</sub> spots to be  $24^\circ$ , which means graphene and MoS<sub>2</sub> were rotated  $24^\circ$  with respect to each other. Additionally, in contrast to graphene/h-BN heterostructure, Moire pattern wasn't observed in graphene/MoS<sub>2</sub> heterostructures due to the atomic number difference between the layers as MoS<sub>2</sub> contrast dominates the image. The red rectangular in figure3(a) shows where EELS map was taken from and also, the spectrum image of the same region are presented in figure3(b) and (c). Both figures represent the same area and the only difference was the contrast as it was intentionally reversed to make heterostructure

(figure3b) and graphene (figure3c) visible. The EEL spectra of the heterostructure side, yellow rectangular in figure3(b) and graphene side, green rectangular in figure3(c) were presented inset figure3(d). Indeed, EEL spectra have proven the presence of graphene and heterostructure. During EELS measurement which was performed in more than a few minutes, we once more observed damage in MoS<sub>2</sub> at the lateral interface similar to the graphene/h-BN heterostructure and not in the basal plane. As a result, it can be inferred that graphene protects the MoS<sub>2</sub> layer from the radiation damage as well [5].



**Figure 3.** STEM-HAADF images of graphene//MoS<sub>2</sub> heterostructure heterostructure, taken at 60kV.

#### 4. Conclusions

In conclusion, graphene/h-BN and graphene/MoS<sub>2</sub> heterostructures were studied via TEM, diffraction and STEM -MAADF and -HAADF imaging. Moire pattern was observed due to the rotation between the graphene and h-BN layers. However, this wasn't found in graphene/MoS<sub>2</sub> heterostructure despite the existing rotation between the layers because of the huge atomic number difference between graphene and MoS<sub>2</sub>. The lateral interface of graphene and the heterostructures was also defined and it was noticed that both h-BN and MoS<sub>2</sub> were damaged at the interface during prolonged imaging due to the weak bonding between the atoms at the edges of the layers as the damage was seen neither in the basal plane of the h-BN nor in the that of the MoS<sub>2</sub>. Additionally, it was revealed that graphene serves as a protecting layer from the radiation damage for h-BN and MoS<sub>2</sub> layer.

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