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Folding two dimensional crystals by swift heavy ion irradiation

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ABSTRACT

Ion irradiation of graphene, the showcase model of two dimensional crystals, has been successfully applied to induce various modifications in the graphene crystal. One of these modifications is the formation of origami like foldings in graphene which are created by swift heavy ion irradiation under glancing incidence angle. These foldings can be applied to locally alter the physical properties of graphene like mechanical strength or chemical reactivity. In this work we show that the formation of foldings in two dimensional crystals is not restricted to graphene but can be applied for other materials like MoS_2 and hexagonal BN as well. Further we show that chemical vapour deposited graphene forms foldings after swift heavy ion irradiation while chemical vapour deposited MoS_2 does not.

1. Introduction

The interaction of swift heavy ions (SHI, ions with energies that are typically around the maximum of the energy loss curve) with matter is based almost exclusively on electronic excitation and ionization processes [1]. Besides basic research, this unique interaction is applied in material research to e.g. create ion-tracks and nanostructures in materials [2,3], surface tracks on insulators [4] or study the radiation hardness of materials [5]. For two dimensional materials however, the experimental and theoretical studies of the interaction with SHI are still sparse. It has been shown that for graphene, an atomically thin layer of carbon atoms, swift heavy ion irradiation under glancing incidence angle can cause foldings in this material [6,7]. Furthermore, it has been shown that SHI irradiation can be used to manipulate the doping level of graphene [8] and the radiation hardness of graphene and MoS_2 devices has been tested [5].

The ability to fold atomically thin materials opens up the opportunity to alter the physical properties of these materials on the nanoscale. In the case of graphene, the folding introduces two changes in the atomically thin sheet. On the one hand the folded area consists of a bilayer which locally strengthens the material [9]. On the other hand, at the point where the material is bent, a close bilayer edge is formed, where the covalent bonds are bent changing the chemical reactivity and transport properties [10]. Because of this a strong magnetophotoelectric effect is expected in graphene foldings [11] as well as bandgap openings [12,13].

In this work, we investigate whether the formation of foldings induced by SHI irradiation is limited to the semi-metal graphene or not. For this other two dimensional materials in form of MoS_2 (direct bandgap semi conductor), hexagonal BN (insulator) and carbon nanomembranes (CNM, a polymeric membrane) have been irradiated and studied using atomic force microscopy (AFM).

2. Experimental

For the ion irradiation experiments single layers of graphene, MoS_2 and hexagonal BN have been prepared by mechanical exfoliation of their respective bulk crystals (HQ Graphene – Groningen, Netherlands) [14]. Prior to the irradiation the thickness of the crystals has been checked by Raman spectroscopy [15–17]. These exfoliated samples were compared to large area two dimensional materials which are commercially available, CVD graphene (Graphenea – Spain, San Sebastian), CVD MoS_2 (HQ Graphene – Groningen, Netherlands) and carbon nanomembranes (CNM Technologies – Germany, Bielefeld). The SHI irradiation were performed at the GANIL (Grand accelerateur d'ions lourds – France, Caen) for the Xe^{23+} irradiation and at the M-branch of the GSI (Gesellschaft für Schwerionenforschung – Germany, Darmstadt) for the U^{28+} irradiation. The samples have been irradiated under glancing

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incidence angle of below 3° with respect to the surface, which is necessary for folding formation [6]. The ion fluence was kept below 10 ions/μm^2 to avoid overlapping foldings. After the irradiation, the samples were analysed using an atomic force microscope (AFM) in tapping mode with standard Si cantilevers (Nanosensors NCHR – Switzerland, Neuchatel).

3. Results

The results of the SHI irradiation of the exfoliated two dimensional crystals are shown in Fig. 1. All three crystals were irradiated under the same conditions (91 MeV Xe^{23+}, incidence angle below 3°) which results in the formation of foldings in each single layer sheet. In graphene (Fig. 1(a)) about 50% of the foldings consists of two folded areas which are positioned parallel to the incident SHI impact. For about 35% an additional third folded area can be observed which is located at the end. Foldings with more than three folded areas are very rare and mostly caused by multiple SHI impacts. The zoom-in shows a typical folding with three folded areas and the corresponding line profile. The line profile reveals a typical height of about 0.7–1.0 nm which is significantly more than the expected height of bilayer graphene [18].

Foldings in single layer MoS_2 show some different characteristics when compared to graphene. No folded areas at the end can be observed and a very large percentage of 80% shows only two foldings. Moreover, for about 13% of the foldings, only one folded area is created. The line profile of the zoom-in (Fig. 1(b)) shows that the height of the bilayer MoS_2 is about 2 nm and the height of the edge is significantly increased to 4 nm. Note, that the edge consists of a closed bilayer edge or half nanotube like structure which is marked in the zoom-in picture.

Compared to graphene and MoS_2, foldings in single layers hBN show a large fraction of incomplete foldings with about 40% of one sided foldings (marked with a white circle) in Fig. 1(c). Furthermore, the amount of folded areas per SHI impact is limited to two and even ruptured foldings can be observed (marked with a red circle). The foldings on hBN show the smallest average height ranging from 0.5 nm to 1.0 nm.

Next, we show that the folding formation is not limited to exfoliated crystals, which have the highest crystalline quality, but can be applied for CVD grown materials as well. In Fig. 2(a) an optical image of CVD grown graphene flake can be seen which has been transferred from a copper foil, where it has been grown on, onto a SiO_2 substrate [19]. The graphene sheet is covering the whole sample, the small dots in the image with a higher contrast are most likely remnants of the transfer process. The Raman spectrum of this graphene sheet shown as an inset in Fig. 2(a) shows a typical spectrum for single layer graphene [15]. The disorder induced D-Peak is almost not present in the Raman spectrum, displaying the high crystalline quality of the CVD graphene sheet [20]. An AFM topography image of the irradiated sample is shown in Fig. 2(b). The CVD graphene sheet folds upon SHI irradiation comparable to exfoliated graphene. The foldings do not look as uniform as on the exfoliated sample in Fig. 2(a). This is most likely caused by the higher surface roughness of the CVD graphene sheet with a rms of 1.5 nm compared to the 0.5 nm of the exfoliated graphene flake and the occurrence of wrinkles which locally cause heavy stress in the CVD graphene sheet [21].

In contrast to graphene, MoS_2 can be easily grown by CVD directly on the SiO_2 and no transfer step is necessary [22,23]. In Fig. 3(a) an

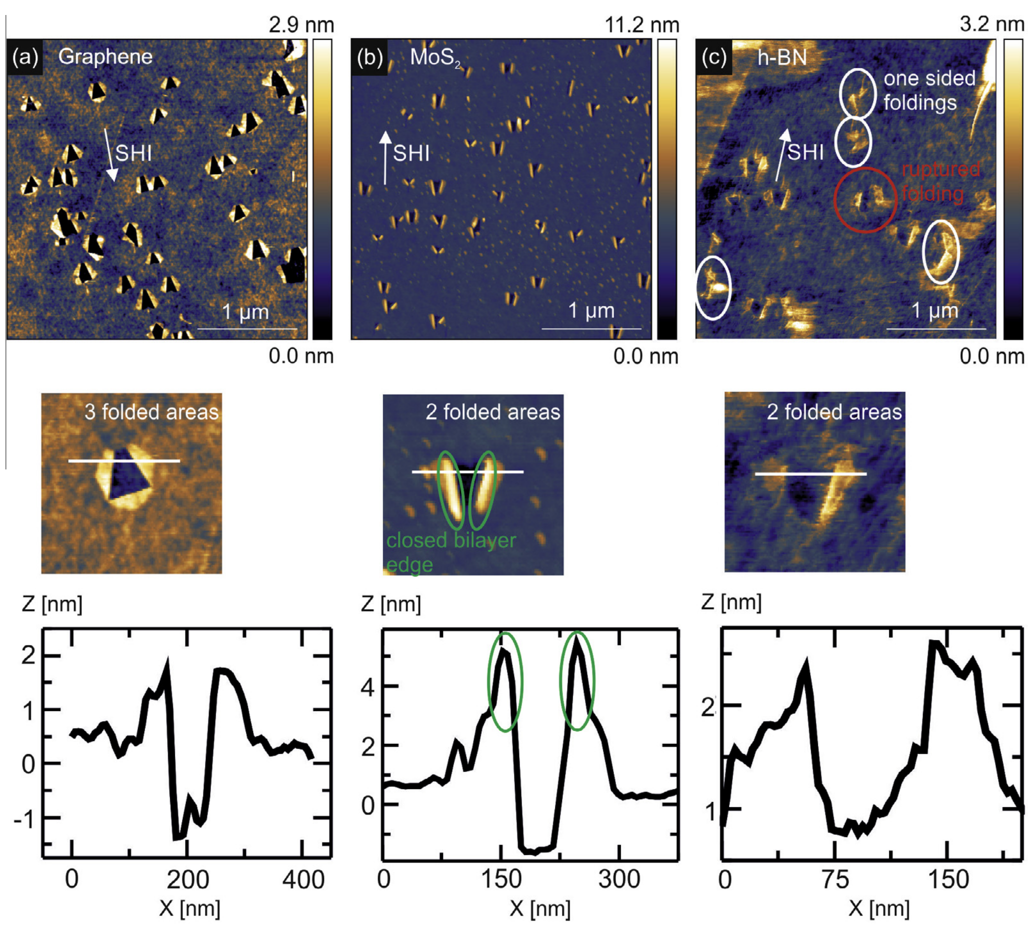

Fig. 1. AFM topography of (a) single layer graphene, (b) single layer MoS_2 and (c) single layer hexagonal BN irradiated with Xe^{23+} ions (E_{kin} = 91 MeV, grazing incidence θ = 1–3°). All three two dimensional materials show foldings upon SHI irradiation.