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Ultra-thin MoS_2 irradiated with highly charged ions

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ABSTRACT

Single MoS_2 layers exfoliated on KBr have been irradiated with highly charged Xe ions, i.e. with Xe^{35+} and Xe^{40+}. By atomic force microscopy (AFM) we identified pits and hillocks induced by single ion impacts. The latter ones appear on single layer and bulk-like MoS_2 after both irradiations, whereas their diameter and height apparently depend on the charge state q and layer number. By comparison of contact mode and tapping mode AFM measurements we deduce that these ion induced defects are topographical hillocks accompanied by an enhanced friction. In contrast to this, pit-like structures were only observed on single layer MoS_2 irradiated with $q = 40$. Taking into account the well known ion induced pit formation on KBr due to defect mediated sputtering, we deduce that pit formation takes place in the substrate and not in the MoS_2 layer.

1. Introduction

It is very well known that ion beams can be used for material modification. Depending on energy, charge state and fluence, these modifications range from the production of isolated point defects to complete phase transitions. Slow highly charged ions (HCI) are the perfect tool for nano-scaled surface modifications as they deposit their energy in a limited volume of a few nm^3 at the impact site. Such ion-induced surface features have been studied on many materials like CaF_2, $SrTiO_3$, graphite and others [1–4]. Despite these experimental efforts, the theoretical understanding of the relevant mechanisms is still rather underdeveloped. A recently discovered class of materials [5] might offer new insights on the details of the interaction. The two-dimensional (2D) forms of several bulk materials show intriguing new properties which differ completely from the bulk properties. For example, the 2D form of the half-metal graphite, called graphene, is a semiconductor with an unusually high mobility [5] and single layers (SL) of MoS_2 become a direct bandgap semiconductor [6]. Both 2D materials show promising potential for use in next generation transistors but MoS_2 offers the advantages of large on–off current ratio as well as immunity to short channel effects and abrupt switching [6,7]. For the incorporation of MoS_2 in electronic devices it is favourable to have reliable methods for manipulation. For instance, techniques to achieve doping or a controlled introduction of defects could be used to influence the transport properties of MoS_2. Highly charged ions could be the perfect tool to tackle this challenge as they can be tuned to deposit their energy basically only in the 2D material and not in the substrate. Nevertheless, HCI irradiation experiments with this new material class are still scarce [8]. Here, we present first data on HCI irradiated samples consisting of single layer MoS_2 flakes and bulk-like MoS_2 on KBr (100).

2. Experiment

2.1. Samples

For the mechanical exfoliation of MoS_2 in principle any flat and clean substrate would be suitable. The insulators CaF_2 and KBr can both be easily cleaved and in addition have been intensively studied regarding HCI induced defects [2,9–12]. Thus, these substrates may serve as references and allow for easy comparison of defects created in irradiated areas covered by MoS_2 with those created in uncovered areas. Here, we have chosen KBr because the exfoliation of MoS_2 on CaF_2 yields primarily bulk-like flakes of small diameter. In addition, the exfoliation on CaF_2 leaves various contaminants on the surface, which make the unambiguous identification of ion induced defects difficult.

KBr(100) crystals (supplied by Korth Kristalle) of $7 \times 7\ mm^2$ were freshly air-cleaved resulting in atomically flat and clean surfaces. Ultra-thin layers of MoS_2 were exfoliated from a single crystal (supplied by SPI Supplies) under ambient conditions and the resulting flakes were of comparable quality as in the case of graphene on CaF_2 [13]. Typical dimensions of the flakes were of a few hundred nm to several µm and the number of layers range from single layer (SL) MoS_2 to bulk-like MoS_2. Note, that SL MoS_2 has typically an apparent height of ≈ 1.7 nm in AFM contact mode images.

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Ambiguous AFM height data is a well-known artefact in the case of 2D materials [14,15]. Here, we attribute the enhanced height to additional friction (see text below and Ref. [16]). Therefore, the exact number of layers was deduced by identifying a SL with Raman spectroscopy (Horiba LabRam, $\lambda = 632$ nm, power below 5 mW) and then using AFM line profiles or histograms for thicker layers assuming a MoS_2 single layer thickness of 0.8 nm [17].

2.2. Atomic force microscopy

To distinguish between true irradiation effects and possible adsorbates or contaminants, we measured the surface topography by means of atomic force microscopy (AFM) before each irradiation. Moreover, the shape and different layer heights of flakes, selected by optical microscopy beforehand, were analyzed and their exact position on the sample was measured. Knowing the position of suitable flakes, the HCI beam spot could be focused on the corresponding sample area. Thus, there is no need to scan the beam over the complete sample, yielding the opportunity to compare irradiated and unirradiated areas of the same sample. The AFM measurements were done with a VEECO DI 3100 in air using constant force mode with Nanosensors PPP-CONTR cantilevers (nominal tip radius $r < 10$ nm) and typical loading forces of $\approx$30 nN, and in tapping mode with Nanosensors PPP-NCHR cantilevers with nominal tip radius $r < 10$ nm and typical amplitudes corresponding to 1 V. Images are treated (plane subtraction) using WSXM [18].

2.3. Highly charged ions

The samples were irradiated at the Duisburg beamline using an electron beam ion trap (EBIT)[19]. Highly charged ^{129}Xe (pure isotope) ions with charge states from $q = 1$ to $q = 44$ can be extracted with acceleration voltages ranging from 4 to 10 kV and focused by a multi-stage lens system onto the sample with a mean beam diameter of 5 mm. A dipole bending magnet from Danfysik is used for charge separation. The irradiation chamber is equipped with a motorized 5-axis manipulator for exact positioning of the samples. A Faraday cup for beam current measurements and an electron beam heating unit are mounted on the sample holder. The EBIT is operated in pulsed mode delivering e.g. fluxes of 1.5×10^5 ions/s cm^2 for Xe^{40+} and 9×10^5 ions/s cm^2 for Xe^{35+}.

After preparation and characterisation by AFM the samples were brought into the irradiation chamber via a transfer system. The base pressure was 2×10^{-9} mbar in the chamber. The samples were kept at room temperature during irradiation. MoS_2/KBr samples were irradiated with charge states $q = 35$ and $q = 40$ and fluences ranging from 5×10^9 to 2×10^{10} ions/cm^2. The kinetic energy was kept constant for both charge states at 260 keV ($\approx$2 keV/amu). After irradiation the samples were transferred out of the vacuum and the surface topography of the irradiated and unirradiated sample areas was observed by AFM as described.

3. Results

3.1. Irradiation with Xe^{40+}

After irradiation of MoS_2/KBr with Xe^{40+}, corresponding to a potential energy of 38.5 keV, typical contact mode AFM topography images as shown in Fig. 1 were obtained. One can easily recognize the layered structure of the MoS_2 flake. The thin MoS_2 layers follow the substrate in a carpet mode, i.e. the substrates' step edges can often be clearly seen underneath the 2D layers, see e.g. Fig. 3a.

From the AFM images we can identify different types of irradiation induced features, namely *pits* and *hillocks*, see Figs. 1 and 2. Pit-like structures appear exclusively on SL MoS_2, whereas no pits are visible on bulk-like MoS_2. Their area density is much lower than the fluence, i.e. on average roughly every sixth ion creates a pit. Note, that in the KBr substrate the typical pits [12] are not observed (see Section 4 below). In addition to the pits, small hillocks can be seen on the large MoS_2 terraces, see Fig. 1. Their area density is much closer to the area density of ion impacts; they are created with an efficiency of $\approx$85%. The area density of both features together agrees thus well with the nominal fluence.

When analyzing the irradiation induced features, it came to our attention that images obtained in trace and retrace scan direction are not identical (see Fig. 2). On thin MoS_2 layers, (Fig. 2a) hillocks are imaged in trace direction; in retrace direction (Fig. 2b) they appear as small holes. For the analysis we have chosen the trace direction: we find the mean diameter of hillocks on SL MoS_2 is (14.5 ± 1.1) nm (FWHM), their mean height is (0.77 ± 0.01) nm. On bulk-like MoS_2 we find a mean diameter of (8 ± 0.1) nm (FWHM) and a mean height of (0.37 ± 0.01) nm.

The pits always appear as pits but their depth differs in trace and retrace direction (see Fig. 2c). Note, that the height difference between traces, Δz, is roughly the same for the pits as for the KBr substrate and much larger than for MoS_2. The pits have a mean depth of (1.92 ± 0.04) nm and a mean diameter of (27.2 ± 0.8) nm in trace direction, the corresponding values in retrace direction are mean depth (3.26 ± 0.33) nm and mean diameter (29.4 ± 0.8) nm.

3.2. Irradiation with Xe^{35+}

A second sample was irradiated with Xe^{35+}, corresponding to a potential energy of 25.4 keV. There, ion induced features could also be observed on SL MoS_2. In contrast to the irradiation with $q = 40$, only hillocks are created but no pits (see Fig. 3). Again, in contact mode features are imaged as hillocks in trace direction and as holes in retrace direction. After analysis of the defects on SL MoS_2 we find a mean diameter (FWHM) of (13.3 ± 0.6) nm and a mean height of (0.27 ± 0.01) nm, both measured in trace direction.

The apparent difference between trace and retrace images in contact mode makes a detailed analysis of the ion induced defects difficult. In addition, the contact mode images do not show the characteristic ion induced pits in the KBr substrate [2,12]. The latter is probably related to the rather high loading force used here ($\approx$30 nN, in contrast to 2–3 nN used in Ref. [2]), which is suitable to image MoS_2 layers correctly, but seemingly not suitable for imaging KBr. During the analysis we found that scan parameters do significantly influence the imaging results and have to be carefully chosen depending on the material. This can be clearly seen from the contact mode images in Figs. 1–3. The KBr substrate appears smeared out and blurry, while the areas covered by MoS_2 are imaged with good quality. In this work, we focus on the analysis of irradiation defects in MoS_2 layers leading us to choose scan parameters (i.e. high loading forces) appropriate for good MoS_2 images, accepting less good resolution on the KBr substrate.

To confirm our data, we performed additional tapping mode measurements of the sample irradiated with Xe^{35+}. Here, the tapping mode topographic images do show the expected pit-like structures on KBr (see Fig. 3). The mean diameter (FWHM) of the observed pits on KBr is (25.5 ± 0.9) nm, the mean pit depth is (0.85 ± 0.01) nm and the efficiency is close to one. These numbers are in good agreement with extrapolated values from Ref. [2]. In addition, tapping mode images show hillocks in trace and also in retrace direction, which is contrary to the contact mode images.

4. Discussion

The results presented in the previous section show that in the system studied here, four different features can be observed after