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Study of Helium-Ion-Beam-Generated Defects in a Monolayer WS_2 Using Aberration-Corrected Scanning Transmission Electron Microscopy

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With the ability to switch between semiconducting and metallic phases, transition metal dichalcogenide (TMD) monolayers are of great interest for potential applications such as in high-speed electronics [1]. Among other methods, one way to change the phase of TMDs relies on defects [2]. In this report, we employ a focused helium ion beam to generate defects in monolayer WS_2 and demonstrate that tungsten vacancy site defects are ion beam dose dependent. In order to study these atomic scale defects, we used an aberration-corrected scanning transmission electron microscopy (STEM). At the highest dose level, however, we observe the formation of tungsten clusters, potentially stemming from the recrystallization of tungsten since sulfur is more easily displaced from the lattice [3]. Focused helium ion beam processing provides an effective means for finely tuning the defect structure of a monolayer WS_2 and potentially yields novel structures not directly attainable by electron-beam processing alone.

For the experiment, a monolayer WS_2 flake was mechanically exfoliated from a bulk crystal on a silicon/polyvinyl alcohol (PVA)/polymethyl methacrylate (PMMA). The PVA layer was dissolved in water to release the PMMA with the monolayer, and then transferred to a Quantifoil Cu grid [4]. The PMMA was removed by annealing the grid at ambient pressure in an Ar/H_2 mixture at 400 °C for 1 hour [5]. The prepared specimen, with monolayer WS_2 spanning the grid holes, was loaded into a Zeiss Orion Nanofab helium ion microscope (HIM). The helium ion beam (accelerating voltage 25 kV) was then scanned across the monolayer WS_2 in lines with doses ranging from 50 ions/nm up to 50,000 ions/nm. In the HIM, imaging of the monolayer was minimized to avoid additional ion beam damage to the specimen. The entire grid is then baked at 120 °C for 8 hours under vacuum to minimize hydrocarbon contamination and inserted into an aberration-corrected STEM (Nion UltraSTEM200-X) for Z-contrast imaging of the defect structure. High angle annular dark field (HAADF) images were obtained to atomically resolve the defect structures at an accelerating voltage of 60 kV in order to minimize any electron beam-induced defect. In addition, Bruker XFlash energy dispersive X-ray spectroscopy was used to identify the chemical composition near the helium ion beam scanned regions.

Defects generated by the helium ion beam were visible in HAADF-STEM images, as shown in Fig. 1. For the low dose of 50 ions/nm, a single vacancy or adatom of tungsten was observed within 10 nm from the ion beam scanned line. As the total dose increased, the number of defect sites increased and are observed further away from the scanned line, up to about 50 nm. For the high dose of 50,000 ions/nm, the monolayer was irrevocably damaged near the scanned line, with none of the original atomic structure visible in the HAADF-STEM. In addition to the ion beam damage, significant carbon contamination was identified along the scanned line from chemical mapping (data not included here). A higher magnification image of the high dose (50,000 ions/nm) region is shown in Fig. 2 where small crystalline clusters of tungsten are observed with ~2 nm diameter. Although further study is necessary to understand the effect of these defects on the electrical properties of WS_2, HIM is found to be useful in generating local defects in a monolayer WS_2. By controlling the total dose and location of the ion beam, complex defect structure can be fabricated in TMD monolayers [6].

References:

[1] S. Manzeli *et al*, Nat. Rev. Mater. **2** (2017), p. 17033.
[2] Z. Lin *et al*, 2D Mater. **3** (2016), p. 22002.
[3] H.-P. Komsa *et al*, Phys. Rev. Lett. **109** (2012), p. 35503.
[4] G.A. Salvatore *et al*, ACS Nano. **7** (2013), p. 8809.
[5] Y. Ahn *et al*, Mater. Express. **6** (2016), p. 69.

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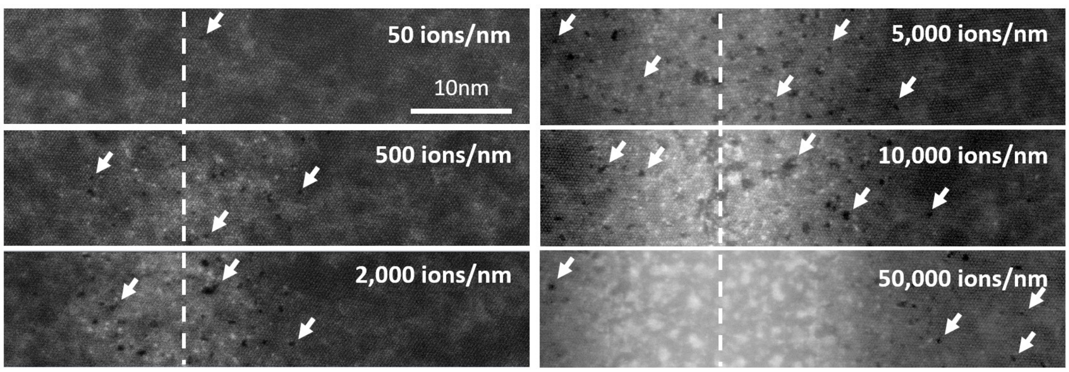

Figure 1. HAADF-STEM images of a monolayer WS_2 with defects generated by helium ion beam. Dash lines are located where the helium ion beam scanned on the specimen. The ion dose is written on the right side of each image. The bright band along the scanned line is showing the carbon contamination from the HIM. Arrows indicate some of the tungsten vacancy sites shown as dark spots in the images. All images are scaled to the top left image. (contrast and brightness adjusted)

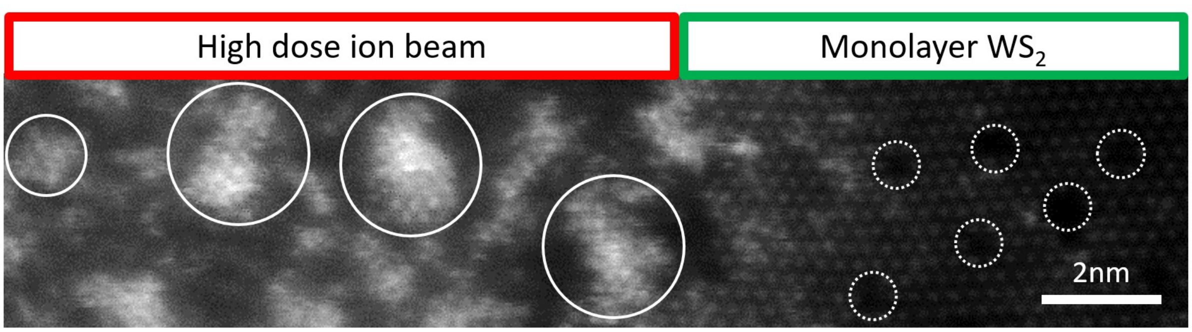

Figure 2. Higher magnification HAADF-STEM image showing the atomic structure near the helium ion beam scanned region with the dose of 50,000 ions/nm. Left side of the image shows where significant ion beam damage was made. Solid circles indicate clusters of recrystallized W atoms (bright intense dots). The dark amorphous region between the clusters are a mixture of W, S and carbon contamination. The right side of the image shows where less ion beam damage was done. Only a few W vacancies indicated with dashed circles are observed with no significant structural change in the monolayer WS_2. (contrast and brightness adjusted)