Microsc. Microanal. 21 (Suppl 3), 2015
doi:10.1017/S1431927615002974 Paper No. 0218

Individual Mo Dopant Atoms in WS_2 Monolayers: Atomic Structure and Induced Strain

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Two-dimensional (2D) materials, including graphene, hexagonal boron nitride and transition-metal dichalcogenides (TMDs), offer a wide range of chemical, optical and electronic properties (*1–4*). 2D semiconducting TMDs, i.e. MoS_2 and WS_2, show layer dependent properties (*5*). For instance, they experience an indirect to direct band gap transition when thinned down to a single-layer (*5*), and also exhibit increased catalytic activity when their thickness is decreased to a monolayer (*6*). WS_2 monolayers, in particular, have shown a great potential for applications in optoelectronic devices (*7*) and hydrogen evolution reaction (HER) (*8*). The unique properties of WS_2 can be further manipulated through substitutional doping. Doping has been used to tune chemical and physical properties of bulk materials, particularly in the semiconductors industry. Dopants can play a more significant role in tailoring the properties of 2D crystals as they are at the surface of the crystal. Importantly, dopants in these monolayer structures can be directly visualized at the atomic-scale using advanced transmission electron microscopes. Understanding how individual dopants interact with the host lattices is the key to modify their physical and chemical properties for future catalysis and device applications. In this work, we use aberration-corrected scanning transmission electron microscopy (STEM) to image the atomic structure of molybdenum (Mo)-doped WS_2 monolayers. Through strain field mapping, we also demonstrate the local strain induced by individual Mo dopants in the host WS_2 lattice.

Single-layers of $W_XMo_{1-X}S_2$ were grown at 800°C using a chemical vapor deposition (CVD) method (*9*). The samples grown on Si/SiO_2 substrates were transferred to gold (Au) quantifoil TEM grids using a poly(methyl methacrylate) (PMMA)-assisted technique (*9*). An FEI Titan^3 60-300 S/TEM at 80 kV was used for STEM imaging. Figure 1a indicates the structural model of a single-layer of $W_XMo_{1-X}S_2$, in which tungsten (W) and Mo atoms share the metal atom sites and are sandwiched by sulfur (S) atoms. Individual Mo dopant atoms were distinguished from the W atoms in the host lattice through Z-contrast imaging using high angle annular dark field (HAADF) STEM. Figure 1b shows the HAADF-STEM image of a single-layer of $W_XMo_{1-X}S_2$, in which two individual Mo atoms can be easily recognized. As the intensity of HAADF-STEM images depends on the atomic number, a higher contrast can be observed for W atoms while Mo atoms are slightly dimmer. The intensity profile obtained from the region in the yellow box in Figure 1c confirms a lower intensity for the Mo atom compared to the W atoms.

Substitutional dopants can locally introduce strain in the host lattice, which can modulate the chemical and physical characteristics of the crystal. For example, the induced strain in these structures can be beneficial for catalysis due to the change in the free energy of chemisorption on the surface (*8*). In this study, we applied geometric phase analysis (GPA) (*10*) to map the strain fields at the dopant sites. We used a symmetric strain matrix to obtain strain fields. The shear strain (ε_{xy}) map presented in Figure 1d, and the superimposed image of the HAADF-STEM micrograph and its ε_{xy} strain map (Figure 1e) clearly confirm the presence of considerable local strain at the Mo atom sites. Such strain fields associated with

the dopants can result in unique chemical, optical and electronic properties in 2D crystals and open up opportunities for novel future applications.

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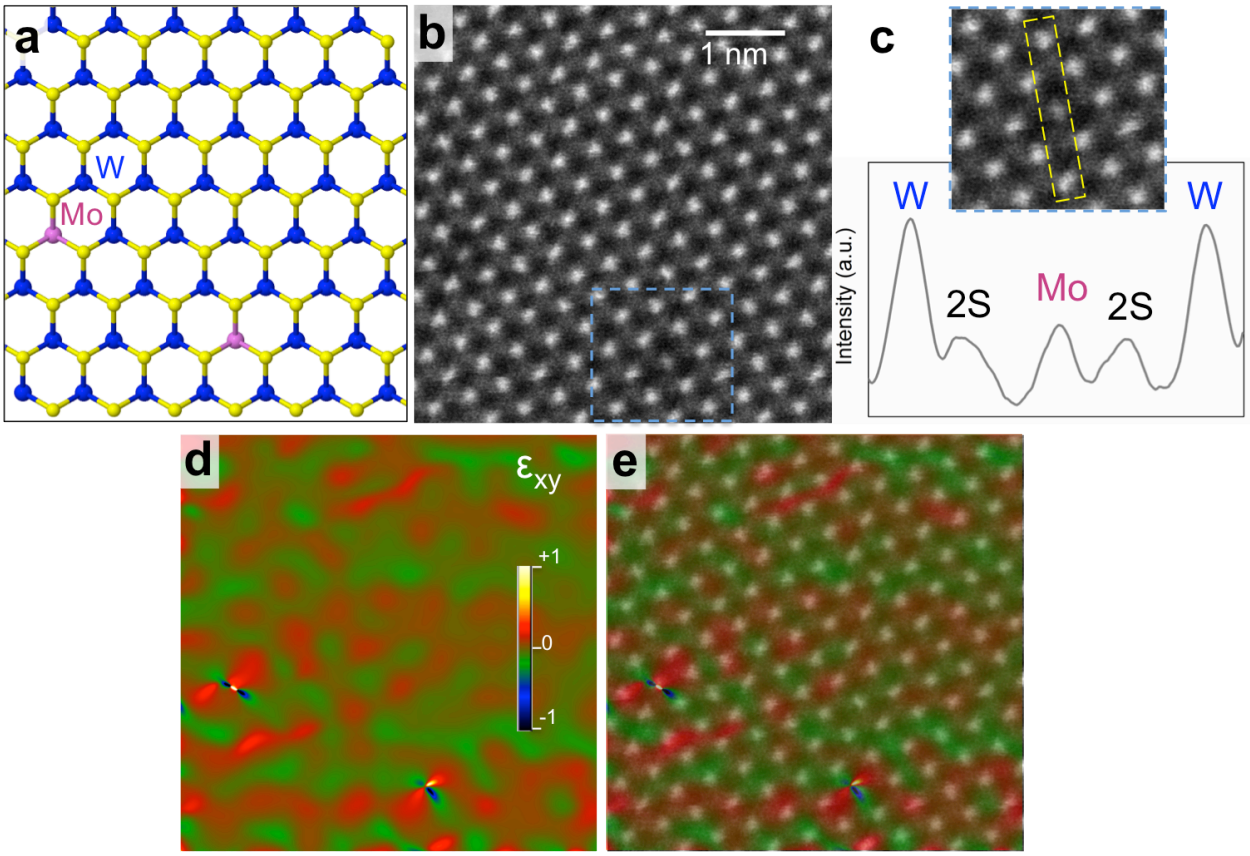

Figure 1. (a) The structural model of a single-layer of $W_XMo_{1-X}S_2$, (b) atomic-resolution HAADF-STEM image of a single-layer of $W_XMo_{1-X}S_2$, indicating W, Mo and S atoms, and (c) the intensity profile obtained from the yellow box region of the HAADF-STEM image. (d) The shear strain (ε_{xy}) map of the monolayered $W_XMo_{1-X}S_2$ (e) and the superimposed image of the atomic-resolution HAADF-STEM image and its ε_{xy} strain map, showing local strain at the dopant sites. The strain color scale (indicated in Figure 1d) ranges from –1 (black) to +1 (white).