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Aberration Corrected High Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM) and *In Situ* Transmission Electron Microscopy (TEM) Study of Transition Metal Dichalcogenides (TMDs)

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It is well documented that the dimensionality of materials plays a crucial role in determining their fundamental properties, in addition to the composition and arrangement of atoms. The most widely studied two-dimensional (2D) material to date is graphene, which exhibits exotic condensed-matter phenomena that are absent in bulk graphite [1]. Research in graphene and the methodology of preparing ultrathin layers has led to the exploration of other 2D materials [2]. In particular, single layers of transition metal dichalcogenides (TMDs) with lamellar structures similar to that of graphite have drawn significant attention because of their tunable bandgaps and abundance [2].

TMDs exhibit diverse properties that depend on their composition, including semiconductors (e.g., MoS_2, WS_2), semimetals (e.g., WTe_2, $TiSe_2$), metals (e.g., NbS_2, VSe_2), or superconductors (e.g., $NbSe_2$, TaS_2). The properties of TMDs also strongly depend on the crystalline structure and the number and stacking sequence of layers in their crystals and thin films [2]. Although electrical, magnetic, and mechanical studies of 2D materials as new material systems have been established, there is a lack of direct atom-by-atom visualization, limiting our understanding of these highly exciting material systems.

Here, we present our recent studies on the characterization of 2D layered materials by means of Scanning Transmission Electron Microscopy (STEM), in particular via the techniques of High Angle Annular Dark Field (HAADF) imaging and *in situ* Transmission Electron Microscopy (TEM). The location and nature of individual atoms, defects, and layer by layer shearing of 2D crystals will be discussed.

We have identified the atomic nature of single layer MoS_2, 2H stacked TMDs (MoS_2, $MoSe_2$, WSe_2, and $MoTe_2$), 1T stacked TMDs (SnS_2, $SnSe_2$, $HfSe_2$, and HfS_2), as well as distorted 1T stacked TMDs (WTe_2) by HAADF STEM imaging. Figure 1 presents HAADF STEM images of the (a) plane view and (b) cross section of 1T stacked $HfSe_2$. In particular, we have successfully imaged distorted 1T stacked TMDs (WTe_2) from three major crystalline orientations and determined the atomic species and their position in this crystal. Combined with first principle calculations, we investigated the characteristic atomic and electronic properties of the material.

The interface and defects of various heterostructures of TMDs such as chemical vapor deposition (CVD) grown MoS_2 on Gr/SiC, molecular beam epitaxy (MBE) grown $HfSe_2$ on MoS_2, molecular beam epitaxy (MBE) grown HfSe on SiO_2, molecular beam epitaxy (MBE) grown SnSe on MoS_2, and molecular beam epitaxy (MBE) grown $Bi_2Se_3/MoSe_2/SnSe_x$ on sapphire have been investigated by HAADF STEM at the atomic scale. These results demonstrate the feasibility and significant potential of fabricating 2D material based heterostructures with tunable band alignments for a variety of nanoelectronic and optoelectronic applications.

Furthermore, we have studied the coexistence of the orthorhombic crystal structure of SnSe and the hexagonal close-packed structure of $SnSe_2$ in a molecular beam epitaxy (MBE) grown tin selenide film. We found that both the defect structure and the local composition fluctuation contributed to the phase transition between $SnSe_2$ and SnSe. This provides an in-depth understanding on the design and synthesis of the $SnSe_2$ heterostructures.

Lastly, we have studied the layer by layer shear exfoliation of a MoS_2 monolayer in a high electric field environment by using an *in situ* transmission electron microscopy nanoprobing technique. Assisted by first principles calculations based on density functional theory, we have demonstrated the ability to extract the zero-load shear strength value of few atomic layers of MoS_2 with the capability of high resolution structural characterization of the sheared interface. Our findings can be used to understand and increase the efficiency of high shear mixing for the industrial production of monolayers from 2D materials, as well as a means to extend our current knowledge of tribology in nanoscale interfaces [3].

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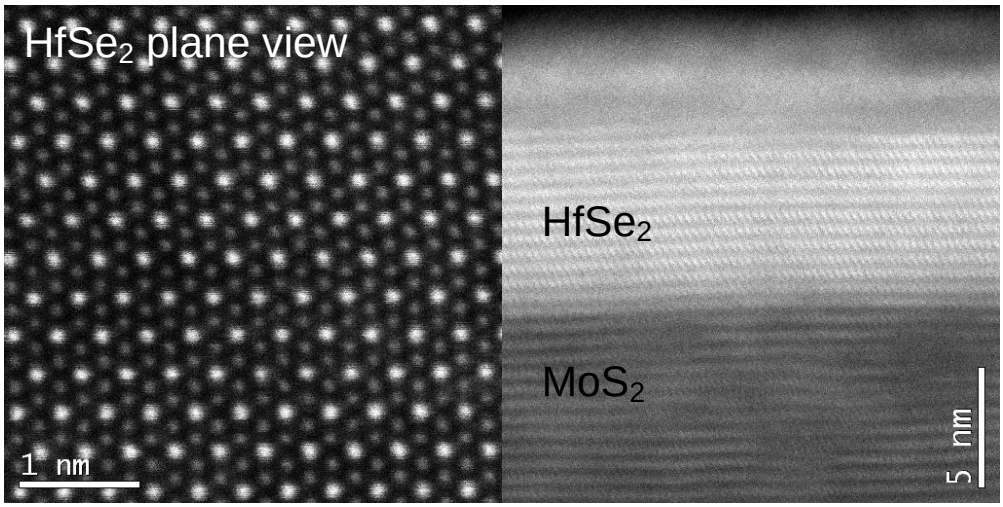

Figure 1. HAADF STEM of the (a) plane view and (b) cross section of 1T stacked $HfSe_2$ on MoS_2