

Thickness and Stacking Sequence Determination of Exfoliated Dichalcogenides Using Scanning Transmission Electron Microscopy

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Layered transition metal dichalcogenides (TMD) have attracted growing interest due to their promise for future technologies. As one approaches the 2D limit, the thickness and local topology can greatly influence the materials macroscopic properties [1]. To understand their potential for electronic applications it is therefore important to identify the dimension and atomic layer stacking of TMDs. The goal of this work is to extract the thickness and stacking sequence of TMDs directly by matching experimentally recorded HAADF images and convergent beam electron diffraction (CBED) patterns to multislice simulations. We demonstrate the accuracy to which thickness and stacking order can be determined in exfoliated TaS₂.

High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) is a powerful technique to image materials such as thin TMDs with atomic resolution (Fig. 1). For exfoliated TaS₂, we observe distinct regions in the same sample exhibiting trigonal structure (Fig. 1a) and hexagonal structure (Fig. 1b), and transitions between the two within approximately 5nm. As illustrated in Fig.1c and Fig.1d, the dramatic change of contrast observed in experimental images can be caused by a bond-length shift of all Ta sites in half the layers. HAADF-STEM image simulations using multislice suggest that the intensity I_2 at Site 2 (labeled in Fig. 1c,d) normalized to the intensity I_1 at Site 1 decreases as the thickness of TaS₂ increases for all-A stacking (Fig. 1e). For the hexagonal structure, produced by shifting about half of the layers (AB stacking), the difference between intensity I_2 at Site 2 and intensity I_3 at Site 3 is suppressed (Fig. 1f) suggesting that the intensity ratios can be used to track layer stacking in thin samples.

An alternative approach to study the structure of layered dichalcogenides is to combine experimental and simulated convergent-beam electron diffraction (CBED) patterns with rich information in the c-axis (i.e. thickness and stacking sequence). We show that the inradius of the hexagonal dark-ring in the first-order diffraction disc decreases as the sample thickness increased (Fig. 2h) for all-A stacking. This enables quantitative determination of the thickness. The accuracy ($\pm 2uc$) of the thickness determination was confirmed by visual comparison (Fig. 2c,d). In addition, CBED patterns exhibit the symmetry of the corresponding structures of TaS₂ in the projection plane (Fig. 3a,b). While uncertainties in the exact stacking sequence remain, the symmetry of the CBED pattern can be used to differentiate between distinct stackings (all-A stacking/AB stacking). Furthermore, variations in the intensity distribution (Fig. 3c,d) and the symmetry of the central disc (Fig. 3e,f) in CBED patterns can be used to determine the thickness and stacking sequence of AB stacking, respectively [2].

References:

[1] Tsen, A. W., Hovden, R., et al. Proc. Natl. Acad. Sci. U.S.A. **112** (2015): 15054-15059.

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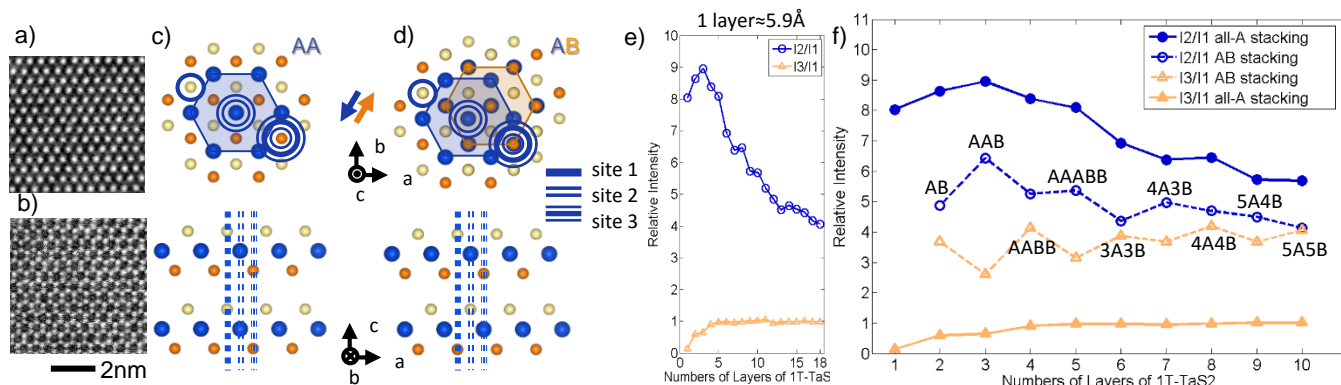


Figure 1. HAADF-STEM image showing a) trigonal and b) hexagonal stacking of Ta sites. c) Illustrations of the structural transition from c) trigonal to d) hexagonal stacking with a one bond-length shift of Ta sites; e) Simulated relative HAADF-STEM intensity of all-A stacking with different thicknesses; f) Effect of layer stacking on simulated relative HAADF-STEM intensity for different sample thicknesses.

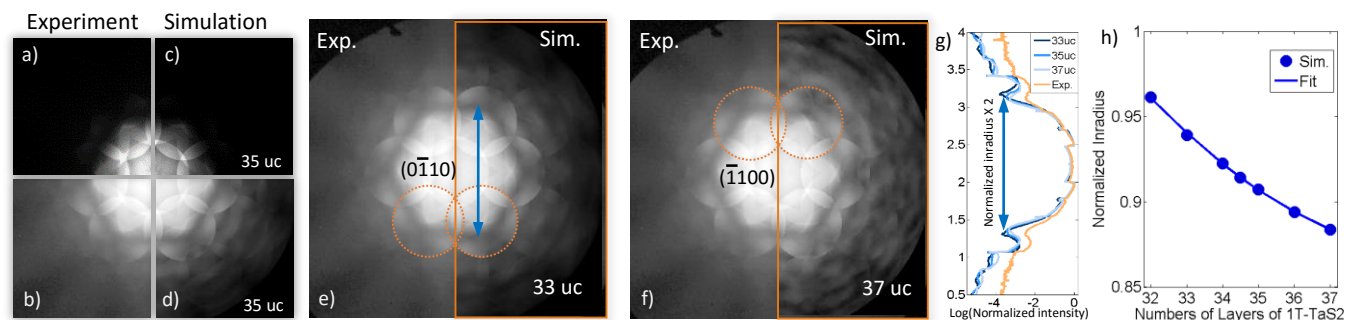


Figure 2. Experimental (a,b) and simulated (c,d) CBED patterns on original (a,c) and logarithmic (b,d) scale. Thickness determination for all-A stacking 1T-TaS₂ by both visual comparisons (a-f) and quantitative methods (g,h). Mismatch between experimental (left half of e,f) and simulated (right half of e,f) hexagonal dark-rings are used for rough thickness determination. g) Line-profile showing simulated CBED intensity at different thicknesses. h) Inradii of the hexagonal ring at different thicknesses are extracted from CBED patterns. The fitting curve can be used to determine sample thicknesses.

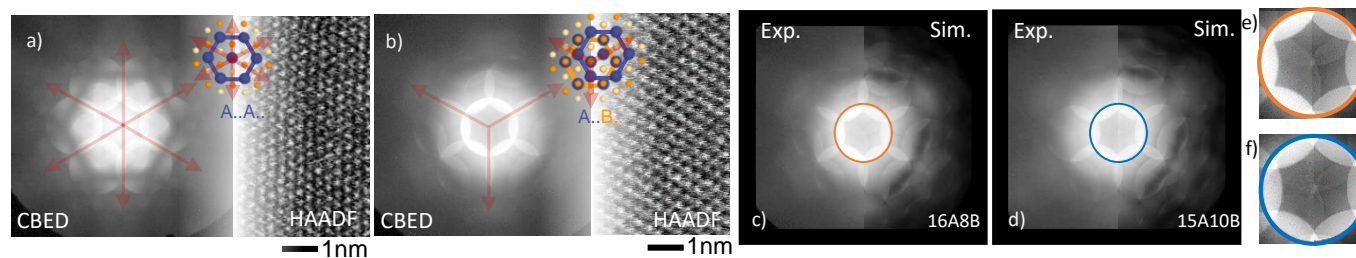


Figure 3. CBED patterns and HAADF-STEM images showing a) trigonal stacking and b) hexagonal stacking of Ta sites. Illustrations of a) all-A stacking and b) AB stacking and correlated CBED patterns showing six-fold/three-fold rotational symmetry. Stacking sequences are determined by visual comparison between experimental (left half of c,d,e and f) and simulated (right half of c,d,e and f) CBED patterns on logarithmic scale and e,f) central discs on original scale for different imaging regions.