

Lattice-Scale Insights for Synthesis and Fabrication of Bespoke Functional Devices

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DECTRIS

ARINA with NOVENA

Fast 4D STEM



DECTRIS NOVENA and CoM analysis of a magnetic sample.
Sample courtesy: Dr. Christian Liebscher, Max-Planck-Institut für Eisenforschung GmbH.
Experiment courtesy: Dr. Mingjun Wu and Dr. Philipp Heide, Friedrich-Alexander-Universität, Erlangen-Nürnberg.

Meeting-report

Lattice-Scale Insights for Synthesis and Fabrication of Bespoke Functional Devices

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Spintronic devices offer the possibility of extremely low-power computation, but depend on the development of novel materials and materials platforms which can be tuned to provide the desired functional properties. One promising materials family for such applications are intercalated van der Waals (vdW) compounds, in which spin-bearing ions can be into the weak-bonding gap between the quasi-two-dimensional layers of the host lattice [1]. For example, metal intercalants such as iron, chromium, or vanadium can be hosted within metallic transition metal dichalcogenides (TMDs) such as TaS₂ and NbS₂, giving rise to a host of magnetic behaviors [2, 3]. Some of these compounds can be stabilized directly through bulk synthesis methods such as chemical vapor transport, but alternative methods to actively and controllably introduce intercalant ions into two-dimensional (2D) TMD crystals offer the potential for fabricating bespoke heterostructures and devices with exquisitely tailored properties. One such approach is soaking 2D crystals in dilute organometallic precursors followed by vacuum annealing. Although previous studies have demonstrated the success of this approach for intercalating 2D TMDs [2], the details of the intercalation mechanism and the relative importance of different parameters within the reaction process have remained elusive. Here, we leverage a suite of advanced analytical techniques within the scanning transmission electron microscope (STEM) to investigate the structural, electronic, and chemical changes in TaS₂ flakes treated with dilute Fe(CO)₅.

Electron energy loss spectroscopy (EELS) provides nano-scale access to the local chemical and electronic environments of the Fe-containing precursor and the intercalated Fe within the TMD flake. Measurements are performed on a probe-corrected FEI Titan Themis CryoS/TEM operating at 120 kV equipped with a low-noise Gatan K2 direct electron detector operated in electron counting mode. To minimize damage under the high-energy electron probe, the sample is cooled with a Gatan 636 liquid nitrogen side-entry holder. We investigate TaS₂ flakes at different stages of the Fe intercalation reaction (Fig. 1, top): 1) reacted with the Fe-containing precursor, 2) reacted with the Fe precursor and annealed for 4 hours at 200°C, and 3) reacted and annealed for 30 minutes at 350°C. The energy loss near edge structure (ELNES) of the Fe-L_{2,3} edge fingerprints the Fe valance in different regions of each sample (Fig. 1, bottom). In all cases, the Fe within the precursor, which remains on the surface of the TaS₂ flake, is consistent with Fe³⁺. Importantly, only the sample annealed to 350°C shows the clear signature of Fe within the TaS₂ flake, with ELNES of the intercalated Fe consistent with Fe²⁺. These results demonstrate the necessity of temperature for driving this reaction.

TMD compounds can stabilize in several structural polymorphs with unique electronic characteristics, but the details of intercalation into these various interfaces have not been systematically explored. Here, we leverage atomic-resolution high-angle annular dark-field (HAADF) STEM imaging to study the intercalation probability between different layers within a heterogenous flake of TaS₂ containing multiple polymorphs (so-called 1T, 2H parallel, and 2H antiparallel, Fig. 2). Cross-sectional HAADF-STEM images are acquired on a Thermo Fisher Spectra 300 X-CFEG operating at 120 kV with a probe convergence angle of 24 mrad. The high-brightness source enables sub-Å spatial resolution even at low accelerating voltage, crucial for resolving the layer and intercalant structure. The intensity profile of the HAADF-STEM image across multiple layers shows subtle differences in the image contrast at the vdW gaps between parallel (P) and antiparallel (AP) stacked layers, suggesting a preference for intercalants to sit between AP stacked layers. Furthermore, quantitative analysis of the interlayer spacing shows a local expansion between the P-stacked TMD layers and a local reduction in interlayer spacing at one type of the 1T-2H (also called 6R) interface. The insights provided by this access to the structural and electronic details of these intercalated compounds provide novel roadmaps for the synthesis and fabrication of entirely unique functional device geometries. [4]

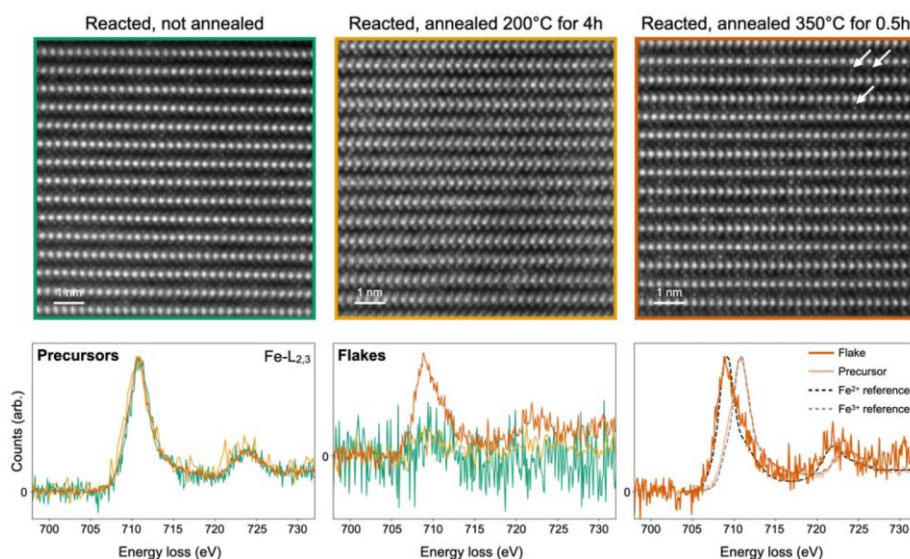


Fig. 1. (top) Cross-sectional HAADF-STEM images of TaS₂ flakes treated with dilute Fe(CO)₅ and subsequently annealed with different conditions. (bottom) ELNES analysis of the Fe-L_{2,3} edge measured locally across just the precursor of each flake shows consistent Fe oxidation in each sample. Spectra acquired from within the flakes only show clear signs of Fe intercalation with heating to 350°C. Comparing spectra in the fully intercalated sample shows a clear change in the Fe valence, consistent with references for Fe²⁺ and Fe³⁺ in the flake and precursor, respectively.

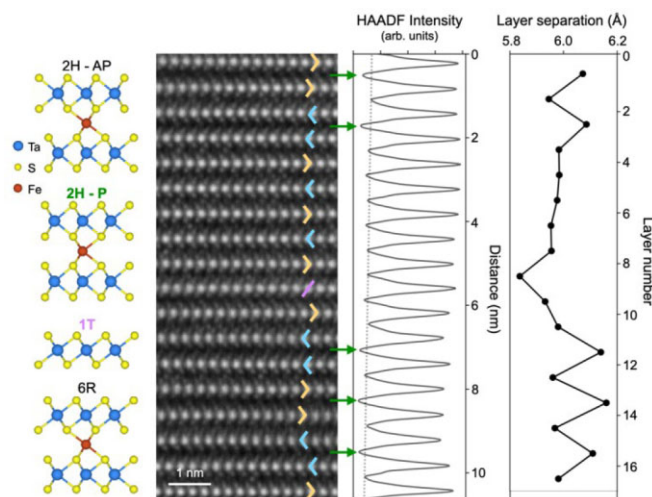


Fig. 2. Different polymorphs and stacking arrangements in TaS₂ are shown by atomic models at left. Cross-sectional HAADF-STEM imaging is used to determine the structure and stacking of each layer; orange and blue chevron overlays indicate opposite orientations of the 2H layer structure, the purple diagonal line denotes a single layer of 1T-TaS₂ within the stack. An integrated line profile across the same HAADF-STEM image shows systematically lower contrast between parallel (P) stacked layers (green arrows). The dashed line is a guide to the eye. The interlayer separation also increases at P interfaces, but decreases on one side of the 1T layer.

References

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4. STEM-EELS characterization was performed at the Cornell Center for Materials Research Facilities supported by National Science Foundation (DMR-1719875). This work made use of the electron microscopy facility of the Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM), which is supported by the National Science Foundation under Cooperative Agreement No. DMR-2039380. B.H.G. was supported by the University of California Presidential Postdoctoral Fellowship Program (UC PFP) and by Schmidt Science Fellows in partnership with the Rhodes Trust. Additional support provided by the Gordon and Betty Moore Foundation EPiQS Initiative (Award no. 10637).