

Direct observation of the interplay between stacking polytypes and self-intercalation in epitaxial Nb_{1+x}Se₂ films

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Background

Stacking and intercalation are crucial for modifying and engineering the properties of two-dimensional (2D) van der Waals (vdW) materials [1, 2]. Stacking, as a control parameter, involves varying the lateral registry or twist angle between adjacent layers to realize, for example, exotic electronic phases in a moiré superlattice [3]. Intercalation refers to the insertion of atoms or molecules into the vdW gap between two layers [4]. This can be achieved by synthetic routes or electrochemistry, potentially leading to emergent superconducting or magnetic states. While the individual potentials of stacking and intercalation have yet to be fully explored, a natural progression is to investigate the synergistic combinations of these two tuning parameters. Understanding the interplay between stacking and self-intercalation is therefore important. However, current knowledge of the interplay between stacking polytypes and intercalation is often based on macroscopically averaged probes, which fail to accurately identify the exact atomic position and chemical state of the intercalants in real space. Atomic-scale observation of the cross section of vdW materials is essential for further clarification.

Methods

In this work, utilizing atomic-resolution electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope, we systematically investigate the atomic and electronic structures and local chemistry in epitaxial transition-metal dichalcogenide Nb_{1+x}Se₂ films grown by "hybrid" pulsed laser deposition and Nb_{1+x}Se₂ crystals grown via chemical vapor transport techniques. Density functional theory calculations were performed to evaluate the roles of thermodynamics and kinetics in these observations.

Results

Using high spatial resolution scanning transmission electron microscopy (STEM), we observe that thin films with an average $x \sim 0.29$ comprise a nanoscale phase mixture of NbSe₂ layers stacked with both 180° and 0° in-plane rotations. The 180°-stacked layers exhibit significant self-intercalation with Nb at the octahedral interstitial sites, likely reaching several tens of percent occupancy, whereas the 0°-stacked layers contain few detectable intercalants at their octahedral interstitial sites. Our findings extend beyond merely imaging intercalants or different stacking structures to establishing a correlative relationship between the two. Density functional theory (DFT) confirms that the energetically favored stacking orientation transitions from 0° to 180° when the self-intercalation exceeds a threshold of approximately $x \sim 0.25$. However, achieving this threshold appears to necessitate kinetic pathways distinct from those in the thin films. Efforts to replicate these observations with Nb_{1+x}Se₂ crystals grown via chemical vapor transport (CVT) yield a homogeneous phase of intercalated, 0°-stacked layers with an average x of at most ~ 0.20 . The presence of Nb intercalants reduces the size of the Fermi hole pockets and suppresses superconductivity in NbSe₂, and these

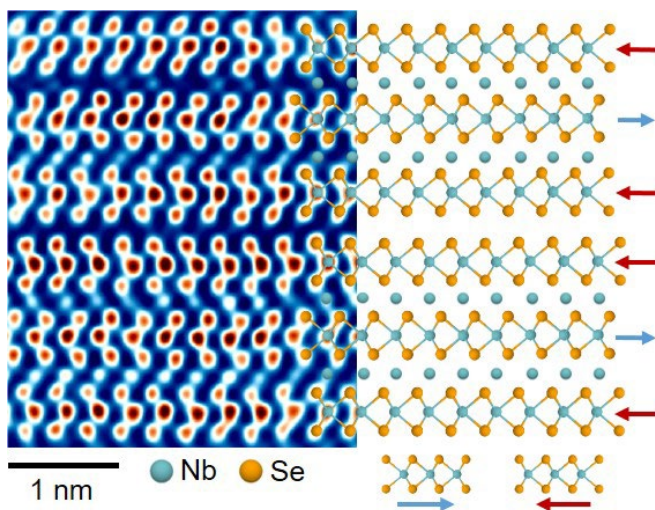
altered properties may provide a foundation for fabricating junctions and nanostructures with more precise control over stacking and self-intercalation.

Conclusion

Using STEM and EELS, we have directly visualized a stacking-selective self-intercalation phenomenon in epitaxial Nb_{1+x}Se₂ films. Our results offer not only renewed mechanistic insights into stacking and intercalation, but also open up prospects for engineering the functionality of TMDCs via stacking-selective self-intercalation. [5]

Fig. 1 stacking-selective self-intercalation phenomenon in epitaxial Nb_{1+x}Se₂ films

Graphic:



Keywords:

STEM, NbSe₂, staking polytypes, self-intercalation

Reference:

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