

# Self-intercalated Ti reveal stacking order in bilayer TiSe<sub>2</sub> films

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Alternatively stacked transition metal dichalcogenides (TMD) may give rise to properties distinct from those of their conventional structures [1]. Different layer stacking can also favor distinct point defects. Proper identification of defects is therefore important for understanding the properties of these materials. Titanium diselenide is a layered TMD with a well-established charged density wave phase [2] and has been studied for its several native defects [3].

Here, STM was used to identify native defects in MBE-grown ultrathin TiSe<sub>2</sub> and to investigate the coexistence of an alternative stacking configuration. In monolayers, surface and sub-surface Se-vacancies dominate. In bilayers, two additional point defects are observed that are separated into domains and are interpreted as Ti self-intercalation defects. The conventional 1T-TiSe<sub>2</sub> stacking cannot account for both defect configurations, suggesting the existence of an alternative stacking. Rotating the top layer 180° about an axis passing through a Se atom at the bottom of the top layer results in the alternative stacking (See Fig.1). In both stacking configurations self-intercalated Ti atoms can occupy the preferred octahedral site, but express different symmetries allowing for discrimination between the stacking in STM images. Finally, sequential thermal annealing revealed a local structural transformation associated with increase of Ti intercalation, forming a 2x2-like periodic superstructure.

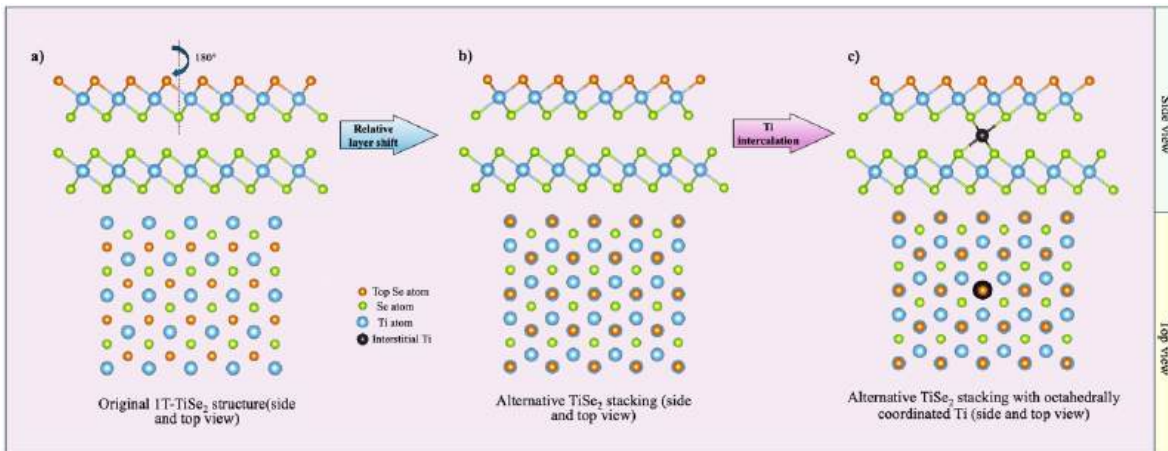


Figure 1. Structural transformation from 1T-TiSe<sub>2</sub> to the proposed alternative stacking structure. a) Regular 1T-TiSe<sub>2</sub>. b) Proposed alternative stacking structure. c) Alternative stacking model containing one octahedrally coordinated Ti interstitial aligned with a top-layer Se atom.

[1] Wang et al., Nat. Commun. 15, 2541 (2024).

[2] Di Salvo et al., Phys. Rev. B 14, 4321–4328 (1976).

[3] Hildebrand et al., Phys. Rev. Lett. 112, 197001 (2014).

## Supplementary Pages

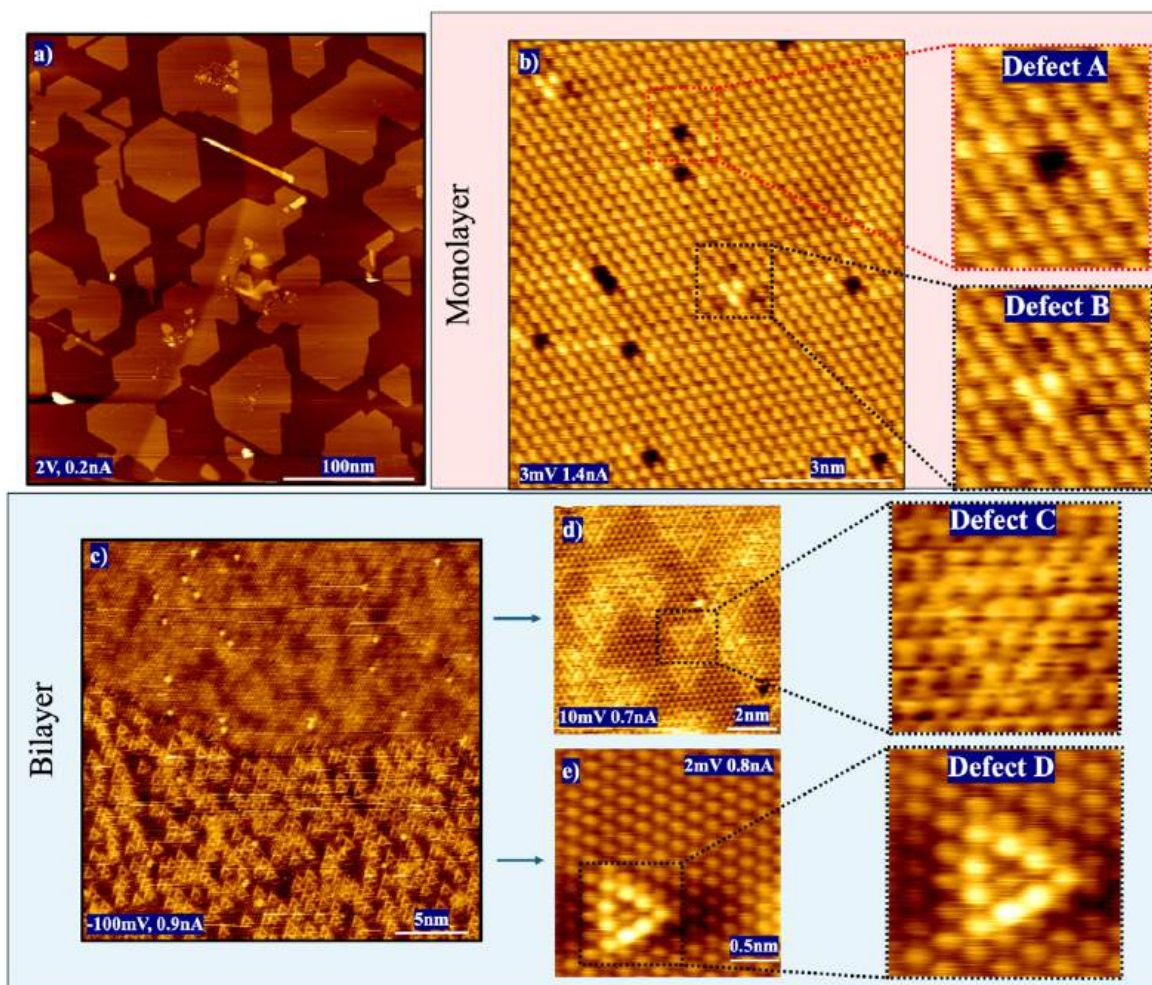


Figure S1 - Surface morphology and point defects in TiSe<sub>2</sub>. a) Large scale STM image of TiSe<sub>2</sub> showing bilayer islands covering approximately 70% of the surface. b) High resolution STM image of the monolayer region exhibiting two different types of point defects, labeled A and B. c) High resolution STM image of two domains within the same bilayer island. The domains are separated by a boundary and contain different point defects. d)-e) High resolution STM images of defects C and D, respectively, observed in different bilayer domains.