Ferroelectric Semiconductors with a Tuneable Inverted Mexican Hat Valence Band

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Van der Waals (vdW) ferroelectrics represent an emergent class of materials for new applications ranging from neuromorphic computing to portable electronics. However, their complex electronic properties have yet to be studied and exploited. Here, we use nanoscale angle-resolved photoemission electron spectroscopy (nanoARPES) and optical transmission in high magnetic fields up to 60 T to reveal the electronic properties of the vdW ferroelectric indium selenide (In_2Se_3) [1]. This semiconductor features an inverted Mexican hat-shaped (IMH) valence band with weakly dispersed energy bands and heavy hole effective masses, which are rarely observed in semiconductors (Fig. a-b-c). The crystal structure and stacking configuration of the individual vdW layers, and the form of the valence band are modified following a thermal annealing of the crystal in ultra-high vacuum, which leads to the conversion of α-In_2Se_3 onto β-In_2Se_3 (Fig d). Since In_2Se_3 possesses intrinsic ferroelectricity [1] and can exist in different vdW polymorphs (α and β) and stacking arrangements of the vdW layers (1T, 2H, 3R) [2], the investigation and fine-tuning of its band structure can underpin the development of systems with ferroic order (e.g. multiferroics with ferromagnetism, ferroelectricity, and ferroelasticity). Also, the *in situ* manipulation of electronic properties and IMH valence band are central to the investigation of carrier correlation phenomena and ferroelectric junctions beyond traditional semiconductors [3-4].

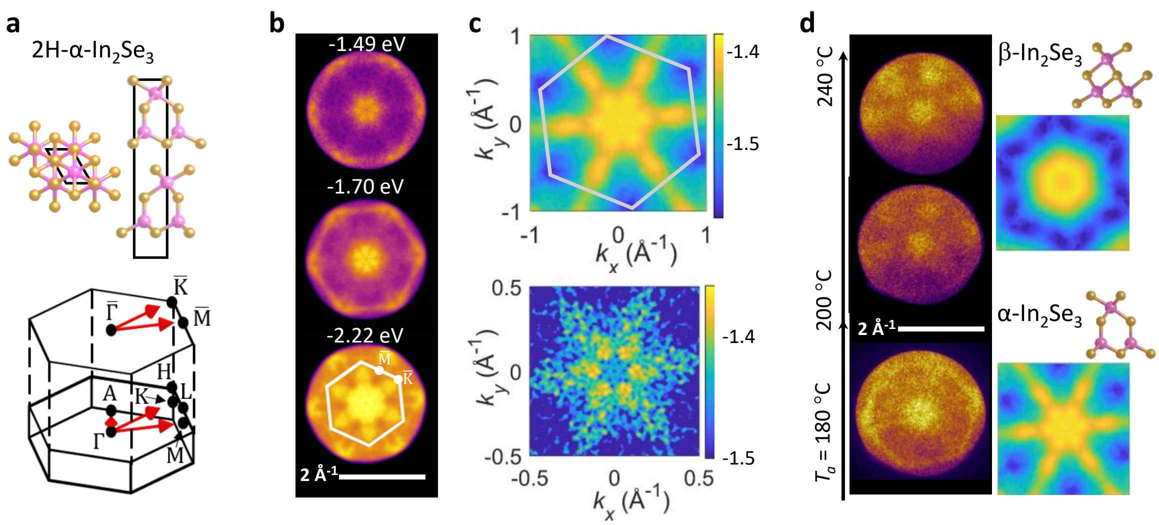

Figure. (a) Side and in-plane view of one layer α-In_2Se_3, and the full and projected Brillouin zone. (b) Constant energy nanoARPES slices taken near the valence band maximum for bulk 2H-α-In_2Se_3 (photon energy 21.219 eV). Energies (in eV) are referenced to the Fermi level. (c) Colour plot of the electron energy (in eV) versus k-vectors, as determined by nanoARPES. Experimental data at the bottom were obtained with greater k-resolution and over a narrower energy range than in the top figure. (d) NanoARPES constant energy slices showing the transition from α to β as the annealing temperature is increased above 180 °C. The insets show the side view of the single vdW layer for the two phases.

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[2] Liu, L. *et al*. *Chem. Mater.* **31**, 10143-10149 (2019).
[3] Xie, S. *et al*. *2d Materials* **8**, 045020 (2021).
[4] Felton, J. et al. unpublished (2024).