Ferroelectric Modulation of Optoelectronic Properties in WSe_2/In_2Se_3 Heterostructures

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Recently, it was discovered that layered In_2Se_3 is ferroelectric with both in-plane and out-of-plane polarizations.[1-2] As compared to traditional ferroelectric materials such as lead zirconate titanate (PZT),[3] the bandgap of In_2Se_3 (~1.3 eV in bulk) is much smaller, which will enable a series of novel devices in ferrophotonic applications. In this work, we investigated the ferroelectric properties of 2D α-In_2Se_3, fabricated ferroelectric photodetectors based on WSe_2/In_2Se_3 heterostructures and studied the impact of ferroelectricity in In_2Se_3 on the photo response properties of the detector.

In ferroelectric materials, the polarization should be switchable by the electric field. To explore the polarization switching, we wrote two square patterns with opposite tip voltages (−7 and +7 V) and measured the PFM in these regions. Fig. 1a and 1b show the topography and phase images of the In_2Se_3 after the write operation. We can see that in the +/-7V region, the phases of In_2Se_3 are about +/-90°, respectively. This result indicates that the polarization in In_2Se_3 can be effectively switched by a vertical electric field. The transport properties of thin In_2Se_3 flakes in the out-of-plane direction were also investigated by conductive atomic force microscopy (CAFM). Fig. 1c shows the current mapping of a ~30 nm thick In_2Se_3 flake after writing with −6 and +6 V rectangular shapes, which clearly show high and low current states, respectively, corresponding to opposite polarization states.

Bulk In_2Se_3 exists in various crystalline phases, including α, β and γ phases. To confirm the crystal structure of our samples, Raman and photoluminescence measurements were conducted. As shown in Fig 1d and 1e, the prominent peak at 180 cm^{-1} in Raman spectrum and the peak at 1.38 eV in the PL spectrum are observed clearly, corresponding to the characteristics of α phase In_2Se_3.

To investigate the impact of the ferroelectricity in In_2Se_3 on the photoresponse, we fabricated photodetectors based on 2D WSe_2/In_2Se_3 heterostructures and measured the photocurrent using a 532 nm laser. The inset in Fig.1f displays the optical image of the WSe_2/In_2Se_3 heterostructure. A laser beam with a spot size of ~4 μm was illuminated on the overlap region of the heterostructure. A photovoltaic phenomenon is clearly observed, which is due to the pn heterojunction formed in WSe_2/In_2Se_3. Here WSe_2 is naturally p-type doped, while In_2Se_3 is naturally n-type doped. Moreover, the open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}) can be tuned by the back-gate voltage, shown in Fig. 1f. When the gate voltage switches from +30 V to -30 V, the V_{oc} changes from positive to negative value, which can be attributed to the change of band slope induced by the back gate voltage in this vertical photodetector. More importantly, the photodetector shows clear memory effect. Fig. 1g shows the drain current at zero drain voltage as a function of time before, during and after applying the ±30 V pulse on the back gate. We can see that the I_{sc} increases after -30 V pulse, while it decreases after +30 V pulse. This phenomenon can be explained by the polarization switching in the ferroelectric In_2Se_3 and the resulting changes in the local electric field. These new 2D ferroelectric heterostructures will provide a unique platform for electro-optic modulators and open up a new path for future optoelectronics and advanced information storage.

References: [1] C. Cui *et al. Nano Lett.* **2018,** *18*, 1253-1258. [2] Y. Zhou *et al. Nano Lett.* ***2017****, 17, 5508−5513.* **[**2] A. F. Scott *et al., Science* **2007,** *315*, 954-959.

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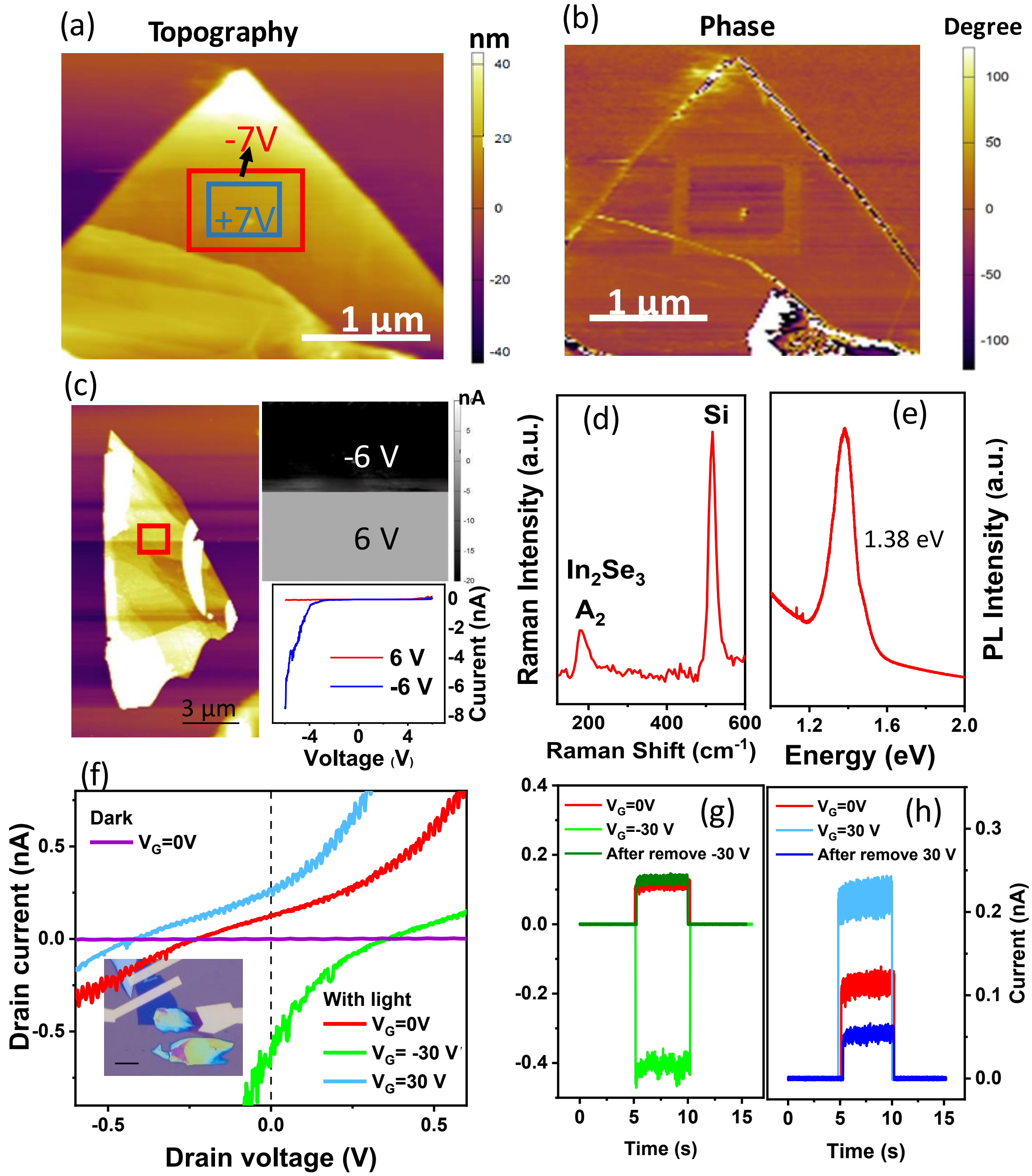

Fig 1. (a) Height image and (b) out-of-plane phase image of In_2Se_3 in PFM measurement. (c) Topography image, current mapping and local IV curves after writing with -6 V and 6 V in CAFM measurement. (d) Raman spectrum and (e) PL spectrum of a α-In_2Se_3 flake. (f) Photocurrent as a function of drain voltage of the photodetector based on WSe_2/In_2Se_3 heterostructure measured at various gate voltages. Inset: optical image of the device. (g) and (h) Short-circuit current as a function of time measured in a photodetector based on the WSe_2/In_2Se_3 heterostructure before, during, and after applied +30 V and -30 V gate voltages.