Supporting Information for

Controlled Growth of Atomically Thin In_2Se_3 Flakes by van der Waals Epitaxy

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Part 1. Methods

1. Characterization of In_2Se_3 flakes

In_2Se_3 flakes were characterized by optical microscopy (OM, Olympus DX51 microscope), scanning electron microscopy (SEM, Hitachi S-4800, acceleration voltage 1-30 kV), atomic force microscopy (AFM, Vecco Nanoscope IIIa), transmission electron microscopy (TEM, FEI Tecnai F30, acceleration voltage 300 kV) equipped with an energy dispersive X-ray spectrometer (EDX). EDX Mapping analysis was taken on a Cs-corrected STEM (TitanG2 80-200 ChemiSTEM equipped with a Super-X EDX detector system), operated at 200 kV using a probe with 50 pA beam current and a converge angle of 21.4 mrad. Electrical measurements were performed in a Micromanipulator 6200 probe station with Keithley 4200 semiconductor analyzer.

2. Selective-area epitaxy of In_2Se_3 flakes

The freshly cleaved mica substrate spin-coated with a poly (methyl methacrylate) (PMMA) film was exposed to the xenon lamp for photolithography using a copper grid or a chrome patterned quartz template as the lithography masks. After exposure, the sample was treated by a developing solution (isopropanol and 4-methyl-2-pentanone, ratio 3:1) and fixing solution (isopropanol) for the development of the PMMA patterns. The mica substrate coated with PMMA patterns was then selectively modified by oxygen plasma etching (90 W, 5 mins). After the PMMA photoresist was removed by acetone and subsequent annealing in air at 550 ^{o}C for 30 minutes, as-pretreated mica substrates were loaded in the tube furnace for the selective-area epitaxy of In_2Se_3 flakes. We found that In_2Se_3 flakes prefer to nucleate and grow epitaxially on the intact mica region rather than the etched region since the chemical and morphological properties of mica are changed after selective-area oxygen plasma etching.

3. The transfer of In_2Se_3 flakes

The atomically thin In_2Se_3 flakes grown on mica substrates can be transferred onto arbitrary substrates using a PMMA-mediated transfer technique.[1] The PMMA solution (MicroChem, 950 kg/mol, ~4 wt.% in anisole) was spin-coated onto In_2Se_3/mica at 2000 rpm for 1 min and baked at 170 ^{o}C for 5 mins to form a thin film that encapsulated In_2Se_3 flakes. A sticky tape with a square hole in the middle was pasted on the surface of PMMA/In_2Se_3/mica, then dip into HF solution (~5%) for about 30 mins to etch away the mica substrate. The PMMA film supported by the sticky tape was attached to the target substrate. After the sticky tape was removed, the PMMA film was dissolved by acetone vapor, leaving the transferred In_2Se_3 flakes on the target substrate (Figure S1A). Figure S1B and S1C show the morphology of In_2Se_3 flakes grown on a mica substrate and after transferred on the SiO_2/Si substrate, respectively.

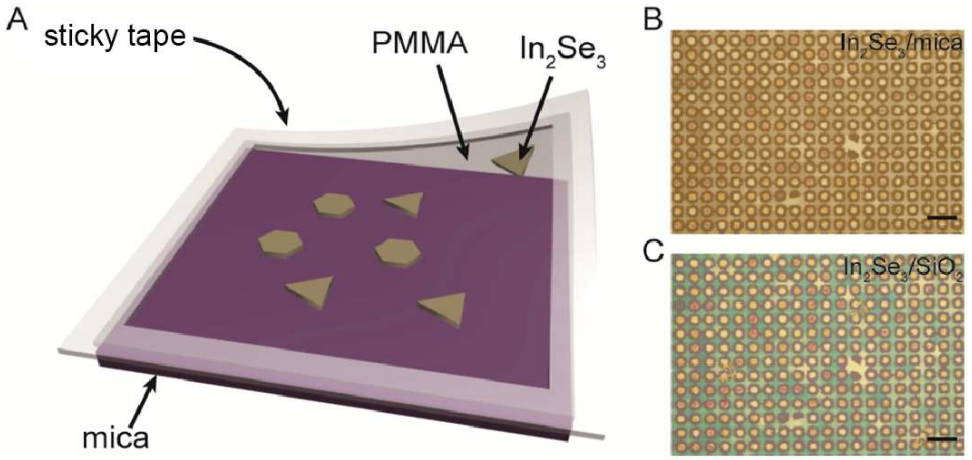

Figure S1. (A) Schematic diagram for the PMMA-mediated transfer technique. (B, C) Optical images of In_2Se_3 flakes before and after transfer, respectively. Scale bars: 20 μm.

4. Device fabrication

The individual In_2Se_3 flakes were transferred onto SiO_2 (300 nm)/Si substrates before electron beam lithography (EBL) was carried out to fabricate alignment markers and microelectrodes. Ohmic contact was made by In/Au (25 nm Cr and 50 nm Au) electrodes via thermal evaporation.

Part 2. TEM and EDX results of In_2Se_3 flakes

The In_2Se_3 flakes were transferred from mica to Cu grid according to the aforementioned method, and then were characterized by a transmission electron microscope (TEM) equipped with energy dispersive X-ray spectrometer (EDX). The elemental mapping images indicate that In and Se elements are uniformly distributed, confirming uniform chemical composition along the entire flake with a In/Se atomic ratio of 2:3 (Figure S2).

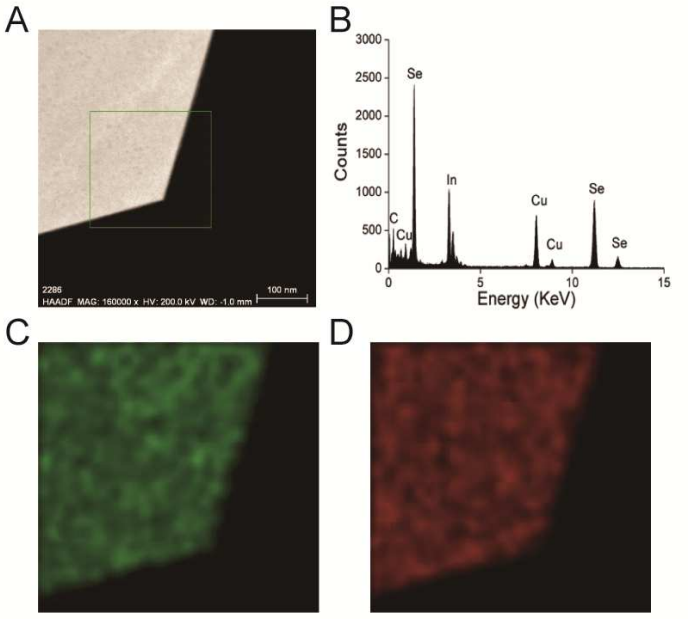

Figure S2. TEM characterization of In_2Se_3 flakes. (A) TEM image of an In_2Se_3 flake. (B) Typical EDX spectrum of the In_2Se_3 flake. The Cu and C signals come from the TEM grid. (C, D) In and Se element maps of the corresponding In_2Se_3 flake, respectively.

Part 3. Phase transition of 2D layered In_2Se_3

We noticed that both the annealing and intensive electron beam irradiation can induce the phase transition of 2D In_2Se_3 flakes. Superlattice-structured In_2Se_3 could transform into simple hexagonal lattice structure after annealing in Ar gas at 300 ^oC. However, if an In_2Se_3 flake with the simple hexagonal lattice structure was exposed to the intensive electron beam irradiation, its local structure can also change to the superlattice structure. Correspondingly, the electrical properties of In_2Se_3 flake changed, depending on the crystal structure.

Figure S3A exhibits an *I-V* curve of the superlattice-structured In_2Se_3 flake with the resistance of 9.5×10^2 Ω. From the *I-V* curve of the same In_2Se_3 flake after the annealing treatment at 300 ^oC (Figure S3B), the resistance changed to 2.0×10^8 Ω, which increased 5~6 orders of magnitude. Interestingly, when the same sample was exposed to electron beam irradiation for a few seconds (Figure S3C), the resistance would decrease from 2.0×10^8 Ω to 2.7×10^6 Ω. We believe that the change of electric properties is related to the local structure of In_2Se_3.[2] The annealing treatment could induce a phase transition from superlattice structure to the simple hexagonal lattice of In_2Se_3, resulting in an increase of the resistance.[2] On the other hand, the intensive electric beam irradiation may induce the formation of superlattice phase, and thus increase the conductivity of In_2Se_3.

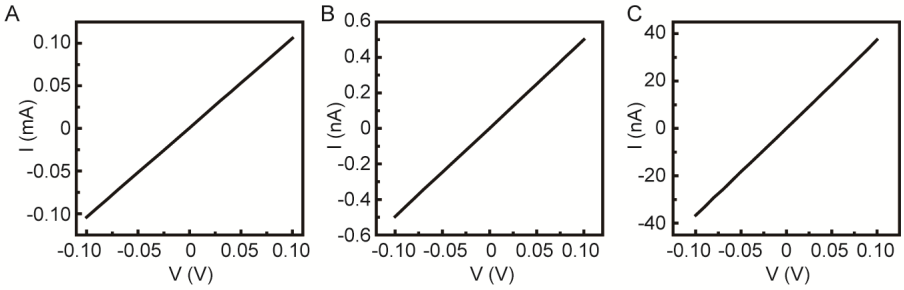

Figure S3. Phase transition of 2D In_2Se_3 flakes induced by annealing and electron beam irradiation: (A) Two-probe I-V measurement of an In_2Se_3 flake with a superlattice structure; (B) Two-probe I-V curve of the same In_2Se_3 flake after annealing; (C) Two-probe I-V curve of the same In_2Se_3 after annealing and electron beam irradiation.

Part 4.

The effect of incident light intensity on photoresponse

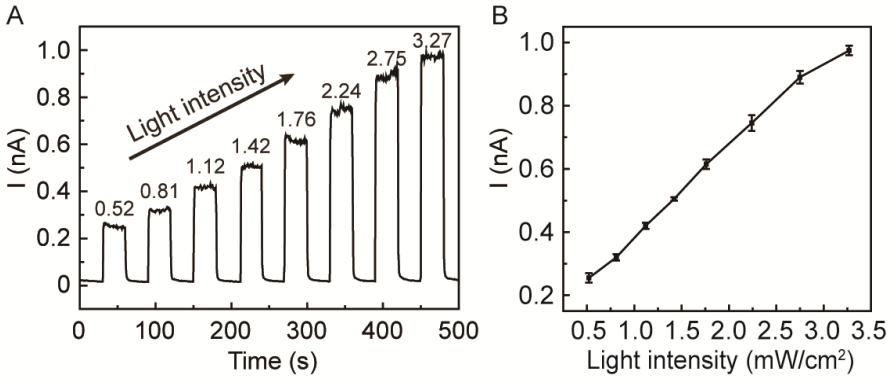

Figure S4. (A) Photocurrent of In_2Se_3 flakes as a function of incident light density. (B) The output photocurrent change with incident light density.

From the photoresponse of In_2Se_3 flakes shown in Figure S4A, we found that the output photocurrent increased when incident light intensity was increased from 0.52 to 3.27 mW/cm^2. As shown in Figure S4B, the photocurrent is linearly proportional to the incident light intensity. The measured current is about 0.24 nA when the light intensity is 0.52 mW/cm^2. Given the active area of ~18.4 μm^2, the corresponding photosensitivity of 2D In_2Se_3 flake is calculated to be about 2.5 A/W.

Reference:

(1) Jiao, L. Y.; Fan, B.; Xian, X. J.; Wu, Z. Y.; Zhang, J.; Liu, Z. F. *J. Am. Chem. Soc.* **2008**, *130*, 12612.

(2) Lai, K. J.; Peng, H. L.; Kundhikanjana, W.; Schoen, D. T.; Xie, C.; Meister, S.; Cui, Y.; Kelly, M. A.; Shen, Z. X. *Nano Lett* **2009**, *9*, 1265.