Supporting Information

Synthesis of Two-Dimensional Alloy $Ga_{0.84}In_{0.16}Se$ Nanosheets for High-Performance Photodetector

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Experimental methods

Synthesis of bulk $Ga_{1-x}In_xSe$ (x = 0.16): Bulk $Ga_{0.84}In_{0.16}Se$ crystals were prepared by the following procedure: Selenium powder (338 mg, 99.99%, Aladdin) and gallium-indium eutectic (300 mg, 75.5% Ga 24.5% In by weight, 99.99%, Alfa) were put in quartz boat, respectively. Then the boat was placed in to a one-zone horizontal furnace with a fused silica tube. The close system was purged with 300 sccm Ar gas for 30 min. Firstly, the boat was heated to 573 K and kept at 573 K for 1 h with 100 sccm Ar/H_2 (V_{Ar}: V_{H_2} = 80:20) as protection gas. Secondly, the boat was heated to 1233 K and kept at 1233 K for 1 h. Last, the system was naturally cooled to room temperature.

Characterizations of $Ga_{0.84}In_{0.16}Se$: The chemical compositions of $Ga_{0.84}In_{0.16}Se$ were determined by energy dispersive X-ray spectroscopy (EDS) (S-4200 Hitachi). The bonding energies of the constituent elements were characterized by high resolution X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo-VG Scientific) with a monochromatic Al Kα radiation source. X-ray diffraction (XRD, DIFFRACTOMETER-6000) pattern was recorded with a Cu Kα radiation source (λ= 0.1542 nm). The microstructures of $Ga_{0.84}In_{0.16}Se$ were measured by transmission electron microscopy (TEM) and selected area electron diffraction (SAED), (FEITECNAI High Resolution TEM operated at 300 kV). The $Ga_{0.84}In_{0.16}Se$ nanoflakes were transferred to lacey support films for the TEM tests by ultrasound in ethanol. The absorption spectrum of the alloy was obtained via a UV−vis−NIR spectrophotometer (UV3600, Shimadzu). Optical images of $Ga_{0.84}In_{0.16}Se$ nanoflakes were taken with an OLYMPUS BX41. The thickness of 2D $Ga_{0.84}In_{0.16}Se$ was determined using atomic force microscopy (AFM, Nanoscope IIIa Vecco). The photoluminescence spectrum was obtained by Raman system

(LabRAM XploRA, 532 nm laser, illumination intensity~1 mW). The stability was taken by thermogravimetric analysis (TGA) (TG 209 F3 Tarsus).

Fabrication and characterizations of $Ga_{0.84}In_{0.16}Se$ FETs and photodetectors: 2D $Ga_{0.84}In_{0.16}Se$ nanosheets were mechanically exfoliated using Scotch tape and transferred onto 300 nm SiO_2/Si substrates. Metal electrodes (Cr = 5 nm, Au = 30 nm) were fabricated by thermal evaporation deposition with a shadow mask. Electronic and optoelectronic characterizations of 2D $Ga_{0.84}In_{0.16}Se$ nanosheets were measured using a semiconductor characterization system (Keithley 4200 SCS) with a Lakeshore probe station. Monochromatic lights of 500 nm, 550 nm, 600 nm, 650 nm and 700 nm were obtained using a 500 W xenon lamp with optical filters. The intensities of incident light source were determined by a power and energy meter (Model 372, Scienteck).

XPS

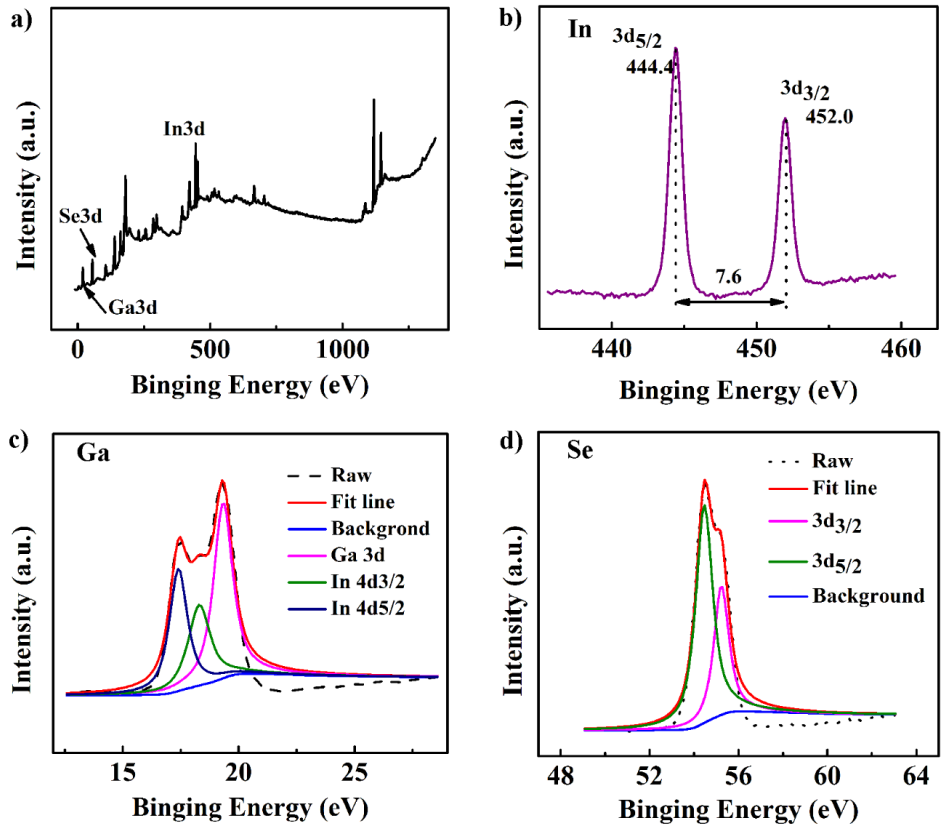

Figure S1. XPS characterization of as-grown $Ga_{0.84}In_{0.16}Se$ sample. (a) Full scale XPS scan of $Ga_{0.84}In_{0.16}Se$. (b) Indium peaks in XPS spectra. (c) Well-resolved Ga 3d and In 4d doublets in $Ga_{0.84}In_{0.16}Se$ sample. (d) Well-resolved Se 3d doublets in $Ga_{0.84}In_{0.16}Se$ sample.

XRD

The main diffraction peaks were indexed to hexagonal structured GaSe single crystal with the lattice constants of a = 3.749 Å and c = 15.097 Å (JCPDS-37-0931). The other diffraction peaks were indexed to hexagonal structured InSe single crystal with the lattice constants of a = 4.005 Å and c = 16.64 Å (JCPDS- 34-1431). The diffraction peaks of GaSe are shifted to a lower diffraction angle corresponding to the increases of lattice constant c, and the diffraction peaks of InSe are shifted to a higher diffraction angle corresponding to the decreases of lattice constant c. This

phenomenon is due to the unit cell of $In_{0.16}Ga_{0.84}Se$ alloy (Ga atoms with In atoms of larger ionic radius) is enlarged and reduced compared to those of GaSe and InSe, respectively.

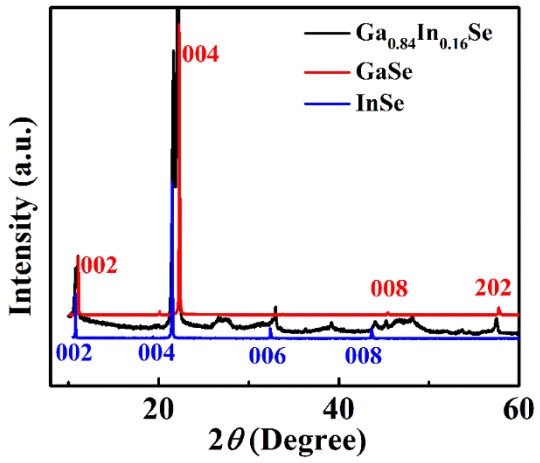

Figure S2. XRD patterns of InSe, GaSe and $Ga_{0.84}In_{0.16}Se$ alloy.

Raman

Raman peaks of 127, 153, 207, 239, 300 cm^{-1} are belonged to GaSe, which is consistent with early report.[2] However, Raman peaks are shifted to lower wave number, which is consistent with XRD results. The peak of 188 cm^{-1} is indexed to E^2 mode of In-Se bond, indicating the successful substitutions of Ga atoms by In atoms.

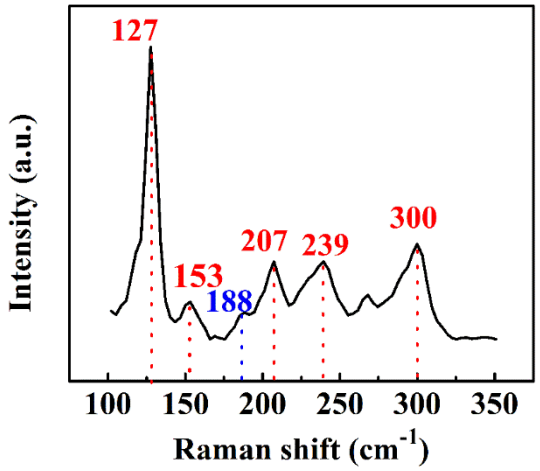

Figure S3. Raman spectrum of $Ga_{0.84}In_{0.16}Se$ alloy.

Optical bandgap

The optical bandgap (E_g) of $Ga_{0.84}In_{0.16}Se$ alloy are estimated from the absorption spectra using the following equation: $ahv = A(hv - E_g)^{n/2}$, where *a*, *h*, *v*, A and E_g are the absorption coefficient, Planck's constant, light frequency, proportionality constant and optical bandgap of the materials, respectively. In the above equation, n is 1 for direct bandgap semiconductors. By extrapolating the linear part of the transformed $(ahv)^2$ *vs (hv)* Tauc plot in Figure 1f inset, the E_g is calculated to be 1.82 eV, which is consistent with PL result.

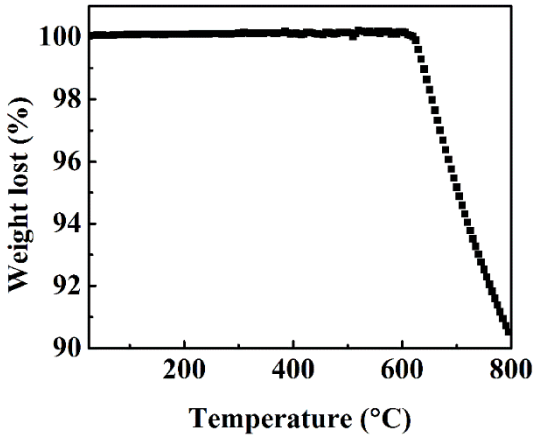

Figure S4. TGA result of $Ga_{0.84}In_{0.16}Se$ alloy.

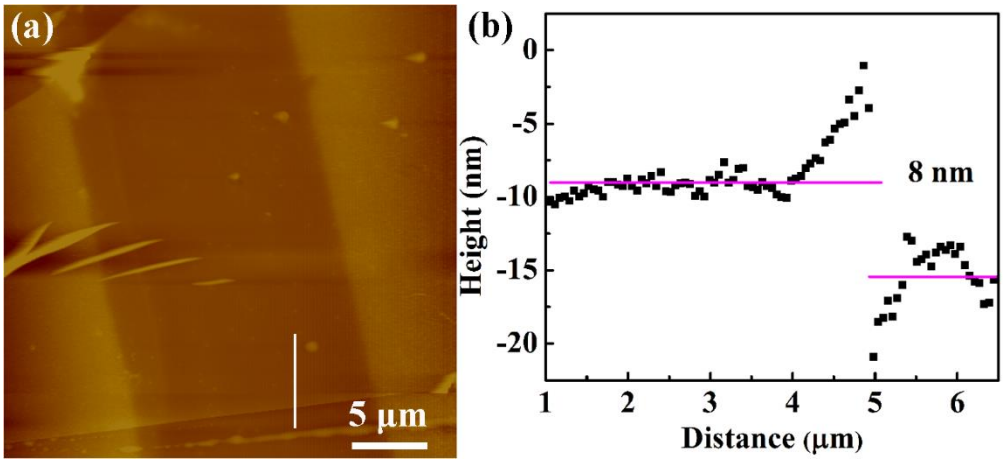

Figure S5. (a) AFM image of 2D $Ga_{1-x}In_xSe$ FETs. (b) Corresponding height profile.

Field-effect mobility and Contact resistance

Field-effect mobility is an another important parameter to assess electronic performance of a FETs, which can be calculated from linear scale of transfer curve using the following equation: $\mu = [L/(W\times(\varepsilon_0\varepsilon_r/d)\times V_{ds})]\times dI_{ds}/dV_g$, where L is length of channel, W is width of channel, $\varepsilon_0 = 8.854 \times 10^{-12}$ Fm^{-1} is vacuum permittivity, ε_r is 3.9 for SiO_2 and d = 300 nm is the thickness of SiO_2.

The contact resistance (R_c) of $Ga_{0.84}In_{0.16}Se$-Cr can be roughly evaluated by the linear region of output curves at high positive gate regions with the following equation: $R_{on} = 2R_c$, where the channel is highly conductive and the source-drain current is mainly limited by source and drain contact resistances[1]. The R_c value of $Ga_{0.84}In_{0.16}Se$ alloy are estimated to be 19 MΩ.

Responsivity, detectivity and external quantum efficiency

Responsivity (R) and detectivity (D^*) are two key parameters to evaluate a photodetector. The R is defined as $R = I_{ph}/(PS)$, where I_{ph} ($I_{ph} = I_{illumination} - I_{dark}$) is the generated photocurrent at a specific illumination light, P is illuminated light intensity, S is effective illuminated area.

The D^* can be calculated *via* the following equation: $D^* = RS^{1/2}/(2eI_d)^{1/2}$, where R is responsivity, S is the area of photodetector channel of 450 μm^2, e is the electron charge of 1.6×10^{19} C and I_d is the dark current.

External quantum efficiency (EQE) is another important parameter for a photodetector and can be calculated by following equation: EQE = $hcR/(e\lambda)$, where h is Planck's constant (6.626×10^{-34} J/s), c is speed of light (3.0×10^{8} m/s), R is corresponding responsivity, e is the electron charge of 1.6×10^{19} C and λ is corresponding illumination light wavelength.

Table S1. Comparison of the critical parameters for photodetectors based on 2D GaSe and InSe

Photodetector	R (A/W)	Bias (V)	λ (nm)	Reference
ME GaSe	2.8	5	254	2
PLD GaSe	1.4	2	240	3
PVD GaSe	0.03	10	Visible light	4
ME InSe	12.3	10	450	5
ME $Ga_{1-x}In_xSe$ alloy	258	5	500	Our work

ME: mechanical exfoliated; CVD: chemical vapor deposition; PLD: pulsed laser deposition; PVD: physical vapor deposition.

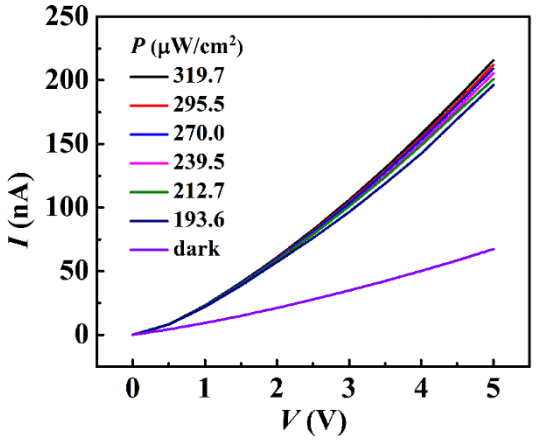

Figure S6. *I-V* curves of $Ga_{1-x}In_xSe$ photodetectors illuminated by 650 nm light with various intensities

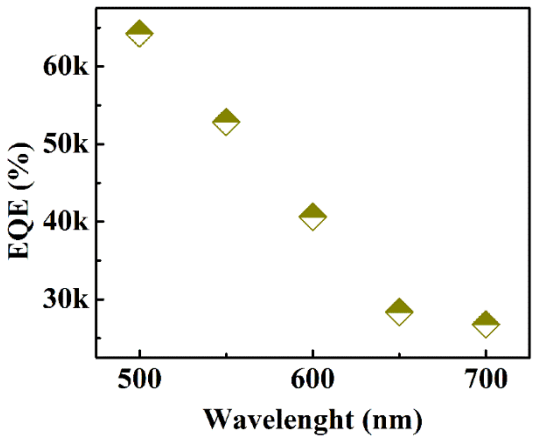

Figure S7. The calculated EQE values illuminated by various lights at V = 5 V.

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