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Defect-induced broadband photodetection of layered γ-In₂Se₃ nanofilm and its application in near infrared image sensor

Chun-Yan Wu, Jing-Wei Kang, Bin Wang, Hui-Nan Zhu, Zhong-Jun Li,* Shi-Rong Chen, Li Wang, Wen-Hua Yang, Chao Xie, Lin-Bao Luo*

In this study, we report on the synthesis of layered γ -ln₂Se₃ for broadband photodetector and near infrared light image sensing application. The layered γ -ln₂Se₃ nanofilm with a thickness of around 74 nm was deposited onto *n*-Si wafer through radio frequency magnetron sputtering. It is found that the as-assembled γ -ln₂Se₃/*n*-Si shows an obvious photovoltaic behavior and can work properly as a self-powered broadband photodetector over a wide range of wavelength (200-2200 nm). Such a unique spectral response beyond the absorption limit of both intrinsic γ -ln₂Se₃ and *n*-Si can be ascribed to existence of defect energy levels between the valence band and conduction band, as a result of Se substitution of In atoms according to theoretical simulation based on first-principles calculations. Specifically, the γ -ln₂Se₃/*n*-Si photodetector has a responsivity of 0.57 AW⁻¹, a specific detectivity of 2.6×10¹² Jones and a fast respond speed (35/115 µs for τ_r/τ_f) under 808 nm light illumination, respectively, which are slightly better or comparable to other devices with similar geometries. Lastly, it was revealed that γ -ln₂Se₃/*n*-Si heterojunction photodetector can function as an effective near infrared (NIR) light image sensor with a decent spatial resolution, which suggests the great potential of the current device in future NIR optoelectronic systems.

Introduction

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Due to strong in-plane covalent or ionic bonds and the weak van der Waals (vdW) interactions in the out-of-plane direction, twodimensional (2D) layered semiconductors have exhibited many attractive characteristics, such as excellent carrier mobility, broad bandgap coverage, outstanding light-material interactions, wonderful flexibility, and layer-dependent electronic and optical properties.^{1,2} By this token, they have shown great potential to address the scaling challenges for traditional silicon-based transistors, which are attractive for miniaturization and highperformance of electronic devices. Till now, a variety of 2D semiconductors beyond graphene, such as transition-metal dichalcogenides (MoS₂, MoSe₂, WS₂, etc.),^{3,4} group III metal chalcogenides (e.g. GaSe, GaS, InSe, and In₂Se₃),⁵⁻⁷ and IV-VI compounds (e.g. SnSe₂,⁸ and SnSe⁹) have been extensively exploited.

Indium selenide (In₂Se₃) is one of the important group III metal chalcogenides, in which strong covalent bonds exist between In and Se within a single layer of Se-In-Se-In-Se and the two neighboring layers are linked together by weak van der Waals interaction.¹⁰ There are totally five commonly identified polymorphs of In₂Se₃: layer-structured phases (α -phase, β -phase and κ -phase formed by inserting a cationic vacancy plane every three in-layers along the *ab*-direction), defect wurtzite structure (γ -phase) and high temperature phase (δ -phase).¹¹ It undertakes a phase transformation (from α to β) at about

200 °C, providing a possible application in multi-level nonvolatile phase-change memories.¹² The direct bulk band gap (1.45 eV) of α -In₂Se₃ allows both a high absorption coefficient and efficient generation of electron-hole pairs under photo-excitation, which has attracted great attention in applications such as photovoltaics and photodetectors.¹³ Yu et al. first reported the development of UV-vis-NIR photodetector based on exfoliated α -In₂Se₃ nanosheet (~10 nm thick, corresponding to 10 quintuple layers),¹⁴ the as-assembled device showed a significantly improved responsivity of 3.95×10² AW⁻ ¹ at 300 nm with an external quantum efficiency greater than 1.63×10⁵ % at 5 V bias when compared to undoped In₂Se₃ 1D nanowires and thin films.¹⁵ Moreover, Island and his colleagues reported on an In₂Se₃ multilayers photodetector with an ultrahigh responsivity (~10⁵ AW⁻¹) and a specific detectivity of ~3×10¹³ Jones at 640 nm under gate voltage of 30 V.¹⁶ In their work, the intrinsic defects and native surface oxides were believed to act as long-lived trap states, which could trap photo-generated holes and effectively gate the In₂Se₃ multilayers, leading to increased photocurrent. Very recently, high-quality In₂Se₃ monolayer has also been successfully deposited via other methods such as vdWs epitaxy¹⁷ and physical vapor deposition (PVD) method.¹⁸ However, these photoconductive photodetectors always suffered from the poor current on/off ratio (<10) as well as the slow response speed (even up to 9 s¹⁶) due to the absence of *p*-*n* junctions. Recently, Zheng et al. reported a scalable production of β -In₂Se₃/Si heterojunction using pulsed-laser deposition (PLD).¹⁹ The type-II staggered *p-n* junctions were sensitive to a broadband wavelength from ultraviolet (370 nm) to nearinfrared (808 nm) and allowed efficient separation of photoexcited electron-hole pairs, giving rise to a decent current on/off ratio (~600) and a faster response speed (<8.3 ms). Fan et al.²⁰ fabricated a

School of Electronic Science and Applied Physics, Hefei University of Technology, Hefei Anhui 230009, P. R. China. E-mail: <u>zjli@hfut.edu.cn</u>, <u>luolb@hfut.edu.cn</u> Electronic Supplementary Information (ESI) available. See DOI: 10.1039/ x0xx00000x

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heterojunction photodiode formed by γ -In₂Se₃ nanoflower film and *n*-Si, which worked well as a self-powered photodetector over the wavelength range from 300 nm to 1100 nm and showed a remarkable photoresponse with an on/off ratio as high as 1570 and an improved response speed (175 μ s/226 μ s for rise/fall time, respectively). On the other hand, till now, In₂Se₃-based NIR photodetector beyond the absorption limit of Si has not been reported.

Herein, in this study, we presented a high-performance photodetector by directly depositing layered γ -In₂Se₃ thin films onto *n*-Si substrate through radio frequency (RF) magnetron sputtering. We found that the as-assembled device exhibited typical obvious photovoltaic behavior and can function as a sensitive self-driven photodetector over the broad range of 200-2200 nm. Notably, when the device was illuminated by 808 nm light, the device has a responsivity (*R*), a specific detectivity (D^*) and response speed (τ_r/τ_f) 0.57 AW⁻¹, 2.6×10¹² Jones and 35/115 μ s, respectively, which are comparable to or better than other devices with similar structures. calculations revealed that the First-principles widened photoresponse spectrum beyond the absorption limit of both intrinsic γ -In₂Se₃ and *n*-Si can be ascribed to the Se substitution of In atoms. What is more, the γ -In₂Se₃/*n*-Si heterojunction device can function as an effective NIR image sensor with a decent spatial resolution, indicative of potential application in NIR optoelectronic devices and systems.

Experimental

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Chemicals Materials Synthesis and Device Fabrication

To fabricate the γ -In₂Se₃/*n*-Si heterojunction, a circular window with a diameter of 5 mm was first defined on a pre-cleaned heavily doped *n*-type (100) Si (<0.01 Ω ·cm)/SiO₂ (300 nm) substrate by photolithography. The substrate was then immersed into a BOE solution (HF: NH₄F: H₂O = 3 mL: 6 g: 10 mL) for 5 minutes to remove the SiO₂ insulator layer within the defined area. γ -In₂Se₃ film was deposited onto the substrate via radio-frequency magnetron sputtering for \sim 4.5 min using a high-purity In₂Se₃ ceramic target. Prior to deposition, the sputtering chamber was evacuated to a base pressure of 1.9×10⁻⁴ Pa, after which, Ar gas (99.99%) at a flow rate of 20 standard cubic centimeter per minute (sccm) was used as the working gas. What is more, the distance between the target and the substrate was set to be 5 cm. The sputtering power, deposition pressure and substrate temperature were 80 W, 0.5 Pa and 360 °C, respectively. For effective collection of photo-generated carriers, a layer of chemical vapor deposition (CVD)-grown monolayer graphene was transferred to the top of the heterojunction through the poly(methyl methacrylate) (PMMA)-assisted wet transfer method. Afterwards, In: Ga alloy was pasted onto the back side of n-Si substrate to form Ohmic contact.

Device Measurement and Characterization

The structure and morphology of as-deposited films were analyzed by X-ray diffraction (X'Pert PRO MPD) with Cu K α radiation, atomic force microscopy (AFM, Dimension Icon), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F), fieldemission scanning electron microscope (FESEM, Quanta FEG 250), and energy-dispersive X-ray spectroscopy (EDS, Oxford INCA, attached to HRTEM). X-ray photoelectron (XPS) spectrae were spectroscopy with Al Ka monochromatic source. Raman analysis was conducted using a microscopic confocal laser Raman spectrometer (HR Evolution Horiba) with a 532 nm laser source. The absorption spectrum was recorded on a Shimadzu UV-2550 UV-vis spectrophotometer. Optoelectronic characterization was carried out in ambient conditions at room temperature, using a semiconductor characterization system (Keithley 2400) equipped with a broadband monochromator (SP 2150, Princeton Co.). Laser diodes with wavelengths of 265 nm (Thorlabs M265L3), 365 nm (Thorlabs M365LP1), 808 nm (Tanon UV-100), 1300 nm (Thorlabs M1300L3), 1550 nm (Thorlabs M1550L3), 1650 nm (Thorlabs M1650L4) and 2200 nm (Thorlabs, MDL-H-2200) were also used as the illumination sources. The power intensity of all light sources was carefully calibrated using a power meter (Thorlabs GmbH., PM 100D) before measurement. For transient photoresponse study, a signal generator (Tektronix, TDS2022B) was employed to connect the laser diode to produce pulsed light of varied frequencies, and an oscilloscope (Tektronix, TDS2012B) was used to record the electrical signal.

The First-principles Calculations

The first-principles calculations were studied based on density functional theory within the projector augmented wave method, implemented in the Vienna ab initio simulation package (VASP).²¹ The generalized gradient approximation (GGA) of the Perdew, Burke and Ernzerhof (PBE) were employed to describe the exchange and correlation functional with the partial core correction included. A cutoff energy of 400 eV was chosen for the plane-wave basis set. The structures were fully relaxed until the force components were smaller than 0.01 eV/Å and the convergence criterion of energy was 10^{-5} eV. Frequency dependent real and imaginary dielectric functions were obtained on the basis of the electronic structure, and optical absorption coefficients were calculated. A vacuum region of 20 Å normal to the surface of 2D systems was added so that the interaction between adjacent slabs can be negligible.

Results and discussion

The γ -In₂Se₃/*n*-Si heterojunction photodetector was fabricated by depositing of layered γ -In₂Se₃ nanofilm onto the phosphorus-doped n-type Si substrate via radio frequency magnetron sputtering, after which, a layer of graphene was then transferred onto the γ -In₂Se₃ nanofilm for effective collection and fast transfer of photogenerated carriers (Fig. 1a). The detailed schematic process is shown in Fig. S1. Fig. 1b shows the cross-sectional field emission scanning electron microscopy (FESEM) image of the device, it is obvious that the nanofilm has a relatively smooth surface (The root mean square roughness is 1.02 nm, see Fig. 1c), with a thickness of about 74 nm, which is consistent with height profile obtained from atomic force microscopy (AFM) image in Fig. S2a. The X-ray diffraction (XRD) pattern in Fig. 1d shows remarkable diffraction peaks at 27.5 $^\circ$ and 44.6 $\,\,^\circ\,$, attributable to the crystal planes (006) and (300) of hexagonal defect wurtzite structure γ -In₂Se₃ (JCPDS No. 40-1407).²² The relatively strong *c*-axis signifies a preferential orientation of the obtained layered γ -In₂Se₃ nanofilm. Further Raman spectrum (Fig. 1e and Fig. S2b) reveals that the as-deposited nanofilm is

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homogeneously dominated by a strong peak at ~150 cm⁻¹, and three weak peaks at ~83, 205 and 246 cm⁻¹. According to previous study,²³ the 150 cm⁻¹ was related to the zone center mode of the γ -phase In₂Se₃ crystal and other two peaks at 83 and 205 cm⁻¹ can also be due to the γ -phase In₂Se₃.²⁴ Nonetheless, the Raman peak appearing at 246 cm⁻¹ should be connected to Se-Se bonds,²⁵ suggesting excess of Se atoms.

To study the microstructure of layered γ -In₂Se₃ nanofilm, the obtained sample was then transferred to a Cu grid for high resolution transmission electron microscopy (HRTEM) analysis. As shown in Fig. 1f, well-defined 2D lattice fringes with an inter-planar spacing of 0.35 nm and 0.204 nm due to the lattice planes (110) and (300) of hexagonal γ -In₂Se₃, respectively, can be easily observed, in consistence with the fast Fourier transform (FFT) pattern (the inset of Fig. 1f). Further energy dispersive spectrometer (EDS) spectrum in Fig. S2c reveals that the nanofilm mainly consists of In and Se elements and the elemental mapping result indicate that both In and Se are homogeneously distributed throughout the sample (Fig. 1g, h). The atomic ratio In/Se was deduced to be about 2/3.17, indicative of a selenium-rich composition.

Fig. 2a plots the current-voltage (*I-V*) curves of the γ -In₂Se₃/*n*-Si heterojunction in dark and under 808 nm illumination, respectively. Clearly, the heterojunction exhibited a typical rectifying behavior in dark, which probably originated from the γ -In₂Se₃/*n*-Si heterojunction, as *Ohmic* contact was formed at graphene/ γ -In₂Se₃ structure (Fig. S3). When illuminated by 808 nm incident light (1 mW cm⁻²), the heterojunction displayed a photovoltaic characteristics, giving the open-circuit voltage (*V*_{oc}) of about 0.22 V and short-circuit current (*I*_{SC}) of about 26.5 µA, respectively (Fig. 2b). Such a photovoltaic behavior suggested the possibility for the γ -In₂Se₃/*n*-Si heterojunction device to work as a self-driven photodetector. Time-dependent photoresponse of the heterojunction under zero bias was further characterized and shown in Fig. 2c. The device was highly sensitive to the incident



Fig. 1 (a) Schematic illustration of the γ -In₂Se₃/*n*-Si heterojunction photodetector. (b) Cross-sectional FESEM image of the device. (c) AFM image, (d) XRD pattern and (e) Raman spectrum of γ -In₂Se₃ nanofilm. (f) HRTEM image of γ -In₂Se₃ nanofilm, the inset shows the corresponding selected area diffraction pattern (SAED). (g, h) EDS elemental mapping of In and Se, respectively.



Fig. 2 (a) *I-V* curves of the γ -In₂Se₃/*n*-Si heterojunction in both linear and semi-logarithmic scales measured in dark, the inset shows the photograph of a device on printed circuit board. (b) *I-V* curves under 808 nm illumination (1 mWcm⁻²), the inset shows the magnified photovoltaic behavior. (c) Photoresponse of two devices (γ -In₂Se₃/*n*-Si and graphene/*n*-Si) under 808 nm illumination at zero bias voltage. (d) Photoresponse of the γ -In₂Se₃/*n*-Si device under 808 nm illumination (1 mWcm⁻²) at different bias voltages.

light and could be reversibly switched between high- and lowconductance states, giving a stable and repeatable $I_{\text{light}}/I_{\text{dark}}$ ratio of \sim 2.17×10⁴.It is interesting to note that the photocurrent of the layered γ -In₂Se₃/*n*-Si heterojunction was about 1 order magnitude higher than that of the graphene/n-Si heterojunction (Fig. 2c). This may be attributed to the enhanced absorption of γ -In₂Se₃ nanofilm as well as the strong built-in electric field formed between γ -In₂Se₃ and *n*-Si, which suppressed the charge recombination at the depletion region and facilitated the separation of photo-generated carriers, leading to a low dark current (~1.4 nA) and a high photosensitivity. Further photoresponse at varied reverse voltages in Fig. 2d revealed that photocurrent can increase with the increase of the reverse bias since the larger electric field benefited the separation of photo-generated electrons and holes and restrained the recombination. Additionally, the space charge region of the heterojunction interface can be extended under reverse bias conditions, which allowed more photo-generated carriers to participate in the formation of photocurrent.

Band alignment of γ -In₂Se₃/*n*-Si heterojunction interface was further explored for better comprehension of the above photosensitivity. Fig. 3a presents the absorption of the γ -In₂Se₃ nanofilm which shows a remarkable absorption in the UV-NIR region. The long absorption tail in the NIR region may be associated with the defects existing in as-obtained γ -In₂Se₃ nanofilm, which will be discussed later. From the $(ahv)^2$ versus hv curve plotted in the inset, the optical band gap of γ -In₂Se₃ nanofilm can be deduced to be about 2.09 eV. This value is slightly larger than the reported ones, which may be ascribed to the small grain size in the nanofilm.²⁶ To study the energy band offset of the γ -In₂Se₃/*n*-Si heterojunction interface, the γ -In₂Se₃/*n*-Si heterojunction interface was etched using repeating Ar⁺ ion sputtering until both Se 3d and Si 2p photoelectron peaks were observed in the X-ray photoelectron spectroscopy spectrum (shown in Fig. S4).²⁷ The onset of the valence band maximum (VBM) peak edge of γ -In₂Se₃

 $(E_{\it VBM}^{\it In_2Se_3})$ was determined to be about 0.858 eV (Fig. 3b), which means that the VBM was located 0.858 eV below the Fermi level, revealing p-type conductivity of γ -In_2Se_3 nanofilm.



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(c)

(a.u.)

Intensity

54 56

Fig. 3 (a) Optical absorption spectrum of γ -In₂Se₃ films, the inset shows the plot of $(\alpha h v)^2$ versus photon energy (hv). (b) Valence-band XPS spectra of *n*-Si and γ -In₂Se₃ films. (c) XPS core-level spectra of Se 3d state measured from γ -In₂Se₃ films and γ -In₂Se₃/*n*-Si heterojunction. (d) XPS core-level spectra of Si 2p state measured from *n*-Si substrate and γ -In₂Se₃/*n*-Si heterojunction. (e) Energy band diagram of the γ -In₂Se₃/*n*-Si heterojunction, showing the transfer process of photo-generated carriers upon light illumination. E_c , E_f , and E_v denote the CBM, Fermi level, and VBM, respectively.

102 104

100

n-SiVBM

2 4 6 Binding Energy (eV)

(e)

the

900 1200 1500 1800 Wavelength (nm)

(a.u.)

ntensity

 $\gamma - In_2 Se_3 Se 3d$ (d)

What is more, the Se 3d and Si 2p core level peaks for bulk materials and the heterojunction interface were shown in Fig. 3c-d. The valence band offset (ΔE_V) of the γ -In₂Se₃/*n*-Si can be calculated by using the following equations:²⁸

$$\Delta E_{V} = (E_{Si2p}^{Si} - E_{VBM}^{Si}) - (E_{Se3d}^{In_{2}Se_{3}} - E_{VBM}^{In_{2}Se_{3}}) - \Delta E_{CL}$$
(1)

$$\Delta E_{CL} = (E_{Si2p}^{Si/ln_2Se_3} - E_{Se3d}^{Si/ln_2Se_3})$$
(2)

where $(E_{Si2p}^{Si} - E_{VBM}^{Si})$ was the energy different between Si 2p and VBM in the *n*-Si substrate, $(E_{Se3d}^{In_2Se_3} - E_{VBM}^{In_2Se_3})$ was the energy different between Se 3d and VBM in the γ -In₂Se₃ nanofilm, ΔE_{CL} was the energy difference between the Si 2p (E_{Si2p}^{Si/In_2Se_3}) and Se 3d (E_{Se3d}^{Si/In_2Se_3}) at the γ -In₂Se₃/*n*-Si interface. Based on these values, the valence band offset (ΔE_V) of the γ -In₂Se₃/*n*-Si heterojunction can be deduced to be about 0.31 eV. Moreover, by using the equation below:

$$\Delta E_C = (E_g^{In_2Se_3} - E_g^{Si} - \Delta E_V)$$
(3)

where $E_g^{In_2Se_3}$ and E_g^{Si} denote the bandgap of both γ -In₂Se₃ and *n*-Si respectively, the conduction band offset (ΔE_c) can be calculated to be about 0.66 eV. Band alignment of the heterojunction interface was then shown in Fig. 3e. Apparently, a built-in electric field (depletion region) will be formed in the interface of γ -In₂Se₃/*n*-Si heterojunction with a direction from *n*-Si to γ -In₂Se₃. When illuminated by light with energy higher than the band gaps, the photo-generated electron-hole pairs in depletion region will be rapidly separated toward opposite directions. The photo-generated holes (electrons) will be swept into γ -In₂Se₃ layer (*n*-Si) and subsequently extracted by the graphene (In: Ga) electrode, giving rise to photocurrent at zero bias.

In order to unveil the underlying origin behind the *p*-type conductivity mentioned above, first-principle calculations were then performed to investigate the electronic structures of the γ -In₂Se₃ nanofilm. Since pristine γ -In₂Se₃ with 3 layers (3L) exhibits electronic structure which is similar to that of the bulk (Fig. S5), 2×2 supercells with 3Ls were used for calculation in this work. What is



Fig. 4 Top and side views of 3L γ -ln₂Se₃ in a 2×2 supercell with (a) Se absorption, (b) Se incorporation, and (c) Se substituting In atom, and (d)–(f) the corresponding band structures and (g)–(i) PDOS, the blue balls denote In atoms and the yellow ones denote Se atoms. Moreover, the larger balls denote the doped Se atoms.

more, only three doping schemes including Se absorption, Se incorporation, and substitution of In atom by Se were considered, considering excessive amount of Se from both EDS and Raman analysis result mentioned above. Fig. 4 presents top and side views of the three doped structures in 2×2 supercells together with the corresponding band structures and projected density of states (PDOS). One can see from Fig. 4d-h that γ -In₂Se₃ with Se absorption and Se incorporation possess similar electronic structures to the pristine one. By contrast, when one In atom was substituted by one Se atom (Fig. 4c), a gap state which is located at 0.23 eV above valence band maximum (VBM) appeared (Fig. 4f). Further PDOS in Fig. 4i indicated that this gap state was approximately half occupied and localized on the substituting Se atom and its three nearest ones. Interestingly, such localization of the gap state can be further strengthened in 3×3 supercell of γ -In₂Se₃ with Se substituting In atoms, as shown by band structures, PDOS, and electron density distribution in Fig. S6. In view of its localization, the gap state cannot form a conducting channel. On the other hand, half occupation quality can facilitate electrons to jump from VB to the gap state, producing the p-type semiconducting character of the doped y-In₂Se₃.

Fig. 5a-b illustrate the photoresponse characteristics of the γ -In₂Se₃/*n*-Si heterojunction measured under 808 nm illumination with different irradiation power. One can easily see that the photocurrent increases gradually with the increasing light intensity (5.43-236.6 μ Wcm⁻²). This is reasonable since stronger illumination will give rise to more photo-generated carriers and therefore lead to a higher photocurrent. Similar evolution was also observed in photovoltage. However, when the light intensity was further increased, a saturation in both photocurrent and photovoltage can be observed (shown in Fig. 5c). The dependence of photocurrent on light intensity can be fitted by a general power law $I_{ph}=P^{\theta}$, where θ was the empirical value reflecting the recombination of the photoexcited carriers and determined by the linear relationship of light intensity and photocurrent.²⁹ As plotted in the inset of Fig. 5c, θ was fitted to be

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0.81 and 0.17 in the relatively low light intensity range (from 5.43 $\mu W cm^{-2}$ to 0.314 mW cm^{-2}) and high light intensity range (from 0.314 to 4.76 mW cm^{-2}), respectively. This fitting results suggest a lower recombination ratio at low light intensity due to existence of trap states in the depletion region, 30 and a relatively stronger combination activity at higher light intensity, which may be ascribed to the increased recombination activity arising from the higher density of the photoexcited carriers. 31

To quantitatively evaluate the device performance of the γ -In₂Se₃/*n*-Si photodetector, two key performance parameters, responsivity (*R*, defined as the photocurrent generated per unit power of the incident light on the effective area of a photodetector) and external quantum efficiency (*EQE*, describing the ratio of numbers of outgoing free electrons to the impinging photons) are calculated by the following equations:³²

$$R = \frac{I_{\text{light}} - I_{\text{dark}}}{P_{\text{in}}S}$$

$$EQE = \frac{hcR}{c^2}$$
(5)

where I_{light} and I_{dark} are photocurrent under 808 nm illumination and in dark, respectively. P_{in} is the incident light intensity. *S* is the effective illuminated area (about 0.2 cm² for this device). *h*, *c*, *e* and λ represent Planck constant, speed of light, the elementary electrical charge, and the incident light wavelength, respectively. As plotted in Fig. 5d, *R* decreased as the light intensity increased and



Fig. 5 (a) *I*–*V* curves of the γ -In₂Se₃/*n*-Si heterojunction photodetector under 808 nm illumination with different irradiation power. (b) Time response under various light intensity at zero bias. (c) Photovoltage and photocurrent as a function of light intensity. Inset shows the curves fitted according to power law. (d) Responsivity and *EQE* as a function of light intensity. (e) A single magnified photoresponse curve at the frequency of 3 kHz to calculate the response time. (f) Wavelength-dependent responsivity and specific detectivity in the range 200-1200 nm.

reached 0.57 AW⁻¹ under the light intensity 5.43 μ WGm²_{Art}Besides, the EQE was calculated to be about 88.5% signifying that incident photons can be converted to electron-hole pairs and contributed to the photocurrent.

Specific detectivity (D^*) is another key parameter of a photodetector, which represents the ability of a detector to detect weak optical signals and can be described by noise equivalent power (NEP):³³

$$NEP = \frac{t_n^{2^{2^{1/2}}}}{p} \tag{6}$$

$$D^* = \frac{(S\Delta f)^{1/2}}{NEP}$$
(7)

where $\overline{i_n^{21/2}}$ is the root mean square value of the noise current and Δf is the specific bandwidth. As shown in Fig. S7, the noise spectral density of the photodetector was 9.49×10^{-14} AHz^{-1/2} at the bandwidth of 1 Hz. Therefore, the highest specific detectivity *D** at 808 nm was calculated to be 2.6×10^{12} Jones.

Response speed is the key parameter of the photodetector which reflects the ability to track rapidly changing optical signals. Herein, the transient photoresponse was recorded by a high-frequency digital oscilloscope, and the high frequency optical signal was provided using a laser diode driven by a signal generator. Fig. S8a depicted the photoresponse of the γ -In₂Se₃/*n*-Si heterojunction photodetector to pulsed light of various frequencies from 500 Hz to 3 kHz. Obviously, the device can be reversibly switched between high- and low-conductance states with excellent stability and reproducibility for all switching frequencies and the 3dB bandwidth can be deduced to be about 3.3 kHz from the relative balance $(V_{max}-V_{min})/V_{max}$ as a function of frequency shown in Fig. S8b. To extract the response speed of the γ -In₂Se₃/*n*-Si device, a single magnified cycle at the frequency of 3 kHz was plotted in Fig. 5e, in which the rise time (τ_r) and the fall time (τ_f) were estimated to be about 35 µs and 115 µs, respectively. This relatively fast response speed may be partially ascribed to the γ -In₂Se₃/*n*-Si interface that can swiftly separate the electron-hole pairs. In addition to the fast response speed, the γ -In₂Se₃/*n*-Si device also displays excellent stability in ambient condition (Fig. S9). Further photoresponse characterization observe that the device actually exhibits a pronounced photoresponse of the γ -In₂Se₃/*n*-Si heterojunction in the broad spectral region of 200-1200 nm with a peak response located at around 820 nm (Fig. 5f).

Table 1 compares the key parameters of the γ -In₂Se₃/n-Si heterojunction NIR photodetector with other Si-based photodetectors with similar geometries. Apparently, both R and D* of the present γ -In₂Se₃/*n*-Si NIR photodetector are comparable to some recently reported 2D materials-based photodetector such as MoS₂/Si,³⁴ PtSe₂/Si³⁵ and Bi₂Te₃/Si,³⁶ but are much better than other graphene-based couterpart.³¹ Notably, it also shows a remarkably other improved response speed than In₂Se₃-based photodetectors,¹⁹⁻²⁰ which may be ascribed to the well crystallinity of the as-obtained layered γ -In₂Se₃ film as well as the well-aligned heterojunction interface.

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Table 1. Comparison of key parameters between this work and other Si-based photodetectors.

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Device Structure Measurement conditions R (AW⁻¹) D* (Jones) τ_r / τ_f Ref I /I light dark V=0 V λ=808 nm γ -In₂Se₃/Si 0.57 2.6×10¹² 1.6×10⁴ 35/115 µs Our work 4.35×10-4 ~109 Graphene/Si V=0 V λ=850 nm $\sim 10^4$ 1.2/3 ms 31 V=0 V λ=808 nm $\sim \! 10^{13}$ 3/40 µs MoS₂/Si ~0.3 8×10³ 34 PtSe₂/Si V=0 V λ=808 nm 0.52 3.26×1013 1.5×10⁵ 35Error! 55.3/170.5 µs Rookmark 0.017 2.5×10¹¹ Bi₂Te₃/Si V=0 V λ=635 nm $\sim 3 \times 10^{4}$ 36 ~102 ms 5.67 5.66×10¹³ γ-In₂Se₃/Si V=-1 V λ=808 nm 1.57×10^{3} 20 175/226 µs β -In₂Se₃/Si V=-4 V λ=532 nm 5.9 4.9×10¹² $\sim 6 \times 10^{2}$ 19 <8.3 ms

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Careful comparison of the spectral response of both γ -In₂Se₃/*n*-Si and Si-based devices finds that the spectral photoresponse of the present γ -In₂Se₃/*n*-Si is beyond the absorption limit of Si (~1100 nm). Fig. 6a-c and Fig. S10 displayed the time response of the γ -In₂Se₃/n-Si heterojunction upon DUV (265 nm) and NIR (1064 nm-2200 nm) illumination. All devices showed stable and reproducible response to incident light and the photocurrent increased gradually with the increasing light intensity. Even though R was relatively low in 2200 nm (0.06 µAW⁻¹ at 38.3 mWcm⁻²), the device still showed a steep rise/fall edge with good reproducibility. Notably, the γ - In_2Se_3/n -Si heterojunction showed a remarkably enhanced responsivity compared with that of graphene/n-Si heterojunction, especially in NIR region (shown in Fig. 6d and Fig. S11). We believe this finding should be ascribed to the strong absorption of the asobtained γ -In₂Se₃ nanofilm in the NIR region (Fig. 6e). As a matter of fact, this enhancement in NIR region is due to increase in absorption coefficient after substituting In with Se atoms. Fig. 6f plots the theoretical absorption coefficient of both prinstine γ - In_2Se_3 and γ - In_2Se_3 with Se substituting In atom in a 2×2 supercell G G A P а t -

60 80 Time (s) 3x10 1050 1200 1350 1500 1650 Wavelength (nm) 600 900 1200 1500 1800

Fig. 6 Photoresponse of the γ -In₂Se₃/*n*-Si photodetector under (a) 265 nm, (b) 1550 and (c) 2200 nm, respectively. (d) Responsivity of graphene/*n*-Si and graphene/ γ -In₂Se₃/*n*-Si measured under 980-1650 nm light illumination with the intensity of 1 mWcm⁻². (e)

Absorption spectra of γ -In₂Se₃ nanofilm, planar *n*-Si and γ -In₂Se₃/*n*-Si heterojunction. (f) Theoretical simulation of absorption coefficients of pristine γ -In₂Se₃ and γ -In₂Se₃ with Se substituting In atom in a 2×2 supercell.

level (Compared with HSE06 and GW methods, this theoretical level is practicable for the present large supercell, and can give correct prediction of shift trend of absorption spectra³⁷). It can be seen that the substitution of In by Se atoms can result in a remarkable red shift of absorption region and an enhanced absorption coefficient from visible to NIR region, in agreement with the experimental absorption of γ -In₂Se₃ nanofilm.

Lastly, the capability of the layered γ -In₂Se₃/*n*-Si heterojunction photodetector for spatial-resolved imaging was explored and the schematic of the single-pixel imaging process was shown in Fig. 7a. To perform the measurement, a laser with a wavelength of 1550 nm was employed to shine the lab-build mask with an open "OK" gesture (20 mm×20 mm, shown in Fig. 7b). The photodetector with an effective illumination area of ~1 mm² was set behind the mask and combined to automatic placement system, which can drive the device to progressively scan along the X- and Y- axis with a step size of 1 mm. The current of each pixel was measured and then incorporated into a 2D contrast mapping system. Fig. 7c shows the imaging result after completing the scanning. It is clear that the "OK" gesture can be clearly identified in the contrast map. Although there exists some burrs at the edges of the image, however, we believe this problem can be optimized by further miniaturizing the device and increasing the number of pixels.³⁸ Such a relatively good imaging quality suggests that the present γ -In₂Se₃/*n*-Si heterojunction photodetector may find potential application in future NIR light optoelectronic systems and telecommunications.



Fig. 7 (a) Schematic demonstration of the imaging system. (b) Original print of the "OK" gesture. (c) The corresponding 2D image mapping under 1550 nm illumination.

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Conclusions

In summary, a sensitive broadband photodetector and near infrared image sensor were developed by directly depositing layered γ -In₂Se₃ nanofilm on n-Si via radio-frequency magnetron sputtering. It is found that the as-assembled device exhibited typical photovoltaic behavior and can function as a sensitive self-powered photodetector over the broad range of 200-2200 nm. Specifically, when illuminated by 808 nm light, the device will have a responsivity (R), a specific detectivity (D*) and response speed (τ_r/τ_f) of 0.57 AW⁻¹, 2.6×10¹² Jones and $35/115 \,\mu$ s, respectively, which are comparable to or better than other devices with similar structures. First-principles calculations revealed that the widened photoresponse spectrum beyond the absorption limit of both intrinsic γ -In₂Se₃ and *n*-Si can be ascribed to the Se substitution of In atoms within the crystal structure. Furthermore, the γ-In₂Se₃/*n*-Si heterojunction photodetector also showed great potential for recording NIR imaging sensor with good reliability. These results suggests that the present layered γ -In₂Se₃ nanofilm/*n*-Si heterojunction may find promising application in future IR optoelectronic systems.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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Table of Content

We report on the synthesis of layered γ -In₂Se₃ nanofilm for broadband photodetector and near infrared light image sensing application.

