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Band offset and an ultra-fast response UV-VIS photodetector in γ -In₂Se₃/p-Si heterojunction heterostructures

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High-quality γ -In₂Se₃ thin films and a γ -In₂Se₃/p-Si heterojunction were prepared using pulse laser deposition (PLD). The band offset of this heterojunction was studied by XPS and the band structure was found to be type II structure. The valence band offset (ΔE_v) and the conduction band offset (ΔE_c) of the heterojunction were determined to be 1.2 ± 0.1 eV and 0.27 ± 0.1 eV, respectively. The γ -In₂Se₃/p-Si heterojunction photodetector has high responsivity under UV to visible light illumination. The heterojunction exhibits highly stable photodetection characteristics with an ultrafast response/recovery time of 15/366 μ s. The ultrafast response time was attributed to type II structure band alignment, which was good for the separation of electron–hole pairs and it can quickly reduce recombination. These excellent properties make γ -In₂Se₃/p-Si heterojunctions a promising candidate for photodetector applications.

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1 Introduction

Two-dimensional layered semiconductors exhibit unique physical and chemical properties compared to their bulk counterparts. They have great application prospects in the field of nano-optoelectronic devices and have attracted widespread attention.^{1–4} However, stable high-performance of these two-dimensional layered semiconductor materials based devices has yet to be further explored. In the past decade, layered materials such as metal dichalcogenides (MoS₂,^{5–7} MoSe₂,^{8–10} WS₂,^{11–13} WS₂ (ref. 14–17)), III–VI semiconductors (GaSe,^{18,19} GaS,^{20,21} InSe,^{22,23} In₂Se₃ (ref. 24 and 25)), V–VI semiconductors (Bi₂Te₃ (ref. 26 and 27)) and elemental semiconductors (black phosphorus²⁸) have found useful applications in nanoelectronics and optoelectronics. Of the various chalcogenides, In₂Se₃ is an interesting III–VI n-type semiconductor due to its multiphase and excellent optical properties. It is also known to have at least five crystal forms (α , β , γ , δ and κ). At different temperatures with a specific stoichiometric ratio, different phases and crystal structures can coexist in case of In₂Se₃.^{24,29,30}

Generally, In₂Se₃ is a direct narrow bandgap semiconductor. Multilayered (ML) indium selenide exhibits high electron

mobility, remarkable light absorption efficiency and sensitivity, and good stability which makes it one of the most promising materials for photodetection purposes. Because silicon is a general-purpose substrate for photovoltaic applications, combining In₂Se₃ with mature silicon technology has great potential for the preparation of photoelectric sensors with high detection performance. Current photodetection technology targets multi-spectral (wideband or dual-band) photodetectors for sensing, imaging under atmospheric conditions, object discrimination and optical communication applications.³¹

Up to now, various synthetic approaches have been used to prepare different In₂Se₃ heterostructures. Zhang *et al.* prepared the In₂Se₃/ZnO heterojunction and studied its offset structure.³² Chen *et al.* developed an effective colloidal process involving thermal injection to synthesize uniform nanoflowers consisting of 2D γ -In₂Se₃ nanosheets.³³ Zheng *et al.* prepared a self-assembled broadband β -In₂Se₃/Si photodetector array for weak signal detection.³⁴ Yang *et al.* Prepared the In₂Se₃/Pi nanosheets and studied its photoresponsivity.³⁵ γ -In₂Se₃/Si has emerged as one of the most promising materials for visible photodetection due to its remarkable responsivity and detectivity in a wide range of wavelengths. In this work, a high-quality n type γ -In₂Se₃ thin film was successfully prepared by pulsed laser deposition (PLD). And we studied the valence band offset (ΔE_v) and the conduction band offset (ΔE_c) of the heterojunction.

The γ -In₂Se₃/p-Si heterojunction was prepared by depositing In₂Se₃ on p-Si substrate. The band offset of this heterojunction was studied by XPS. The γ -In₂Se₃/p-Si heterojunction exhibits significant responsivity and detectability over a wide range of wavelength. This heterojunction photodiode exhibits excellent response characteristics as an optoelectronic device.

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2 Experimental

The In_2Se_3 was grown on Si substrate using the PLD method with solid targets of In_2Se_3 (99.99%). The deposition rate was calculated by using thickness of the grown films and deposition time and found to be 0.12 nm s^{-1} . Background vacuum pressure was kept at $1 \times 10^{-4} \text{ Pa}$. 248 nm pulsed line from a Coherent COMPexPro 102 excimer laser was used as laser source. The pulse energy and working frequency were maintained at 200 mJ and 2 Hz, respectively. The substrate temperature was kept at 600°C during growth. At the end of growth, the samples were naturally cooled to room temperature and the sample was taken out to obtain In_2Se_3 /p-Si heterojunction. X-ray photoelectron spectroscopy in this experiment was tested by the Kratos Axis Ultra XPS system. Al $\text{K}\alpha$ ($h\nu = 1486.6 \text{ eV}$) wavelength was used as an X-ray source which can accurately calibrate the work function and Fermi level.

A typical XRD spectrum shown in Fig. 1 is a well-defined set of diffraction peaks for In_2Se_3 . The XRD standard alignment card confirms that these peaks are assigned to the hexagonal phase of In_2Se_3 with lattice parameters: $a = 0.71$, $c = 1.93 \text{ nm}$

Fig. 1 The XRD patterns and the Raman spectrum of the In_2Se_3 .

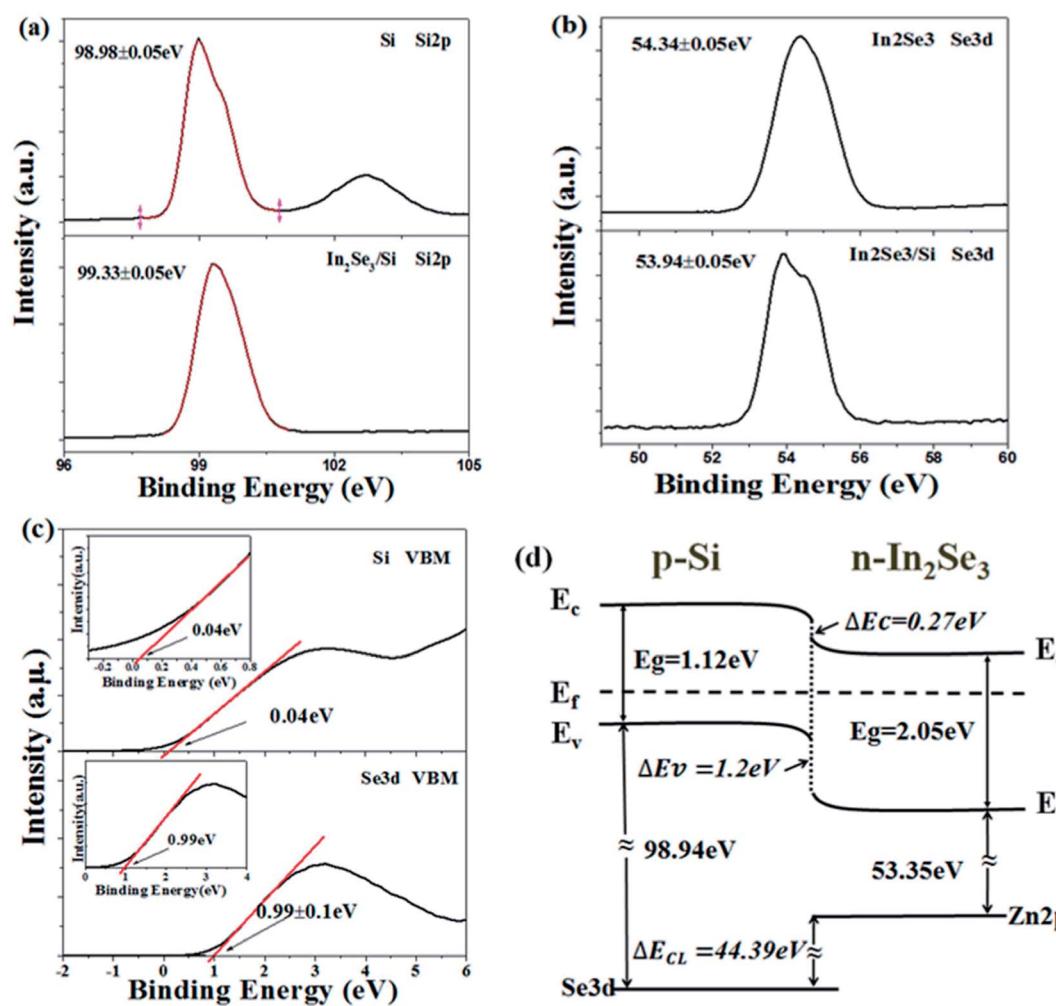
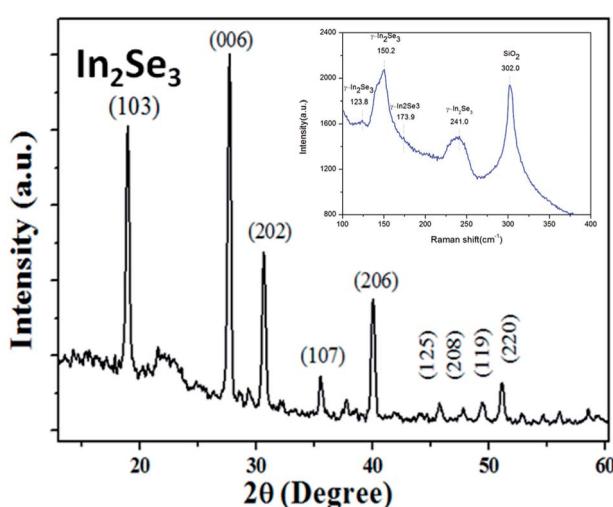


Fig. 2 (a) The XPS CL spectra of the $\text{Zn}2p$ state measured from the Si sample and In_2Se_3 /Si heterojunction, (b) the XPS CL spectra of the $\text{Se}3d$ state measured from the In_2Se_3 films and In_2Se_3 /Si heterojunction, (c) the valence-band XPS spectrum of Si and In_2Se_3 films, and (d) energy band diagram of type-II band alignment of the In_2Se_3 /Si heterojunction.



(JCPDS card, no. 71-0250) which means that it has a gamma phase structure.³⁶ The Raman spectrum of gamma phase In_2Se_3 is shown in the inset of Fig. 1. It exhibits vibration mode at 123.8, 150.2, 173.9, and 241.0 cm^{-1} , which are consistent with previously reported results.³⁰ The vibration mode at 302.0 cm^{-1} is consistent with reported of SiO_2 . The XRD pattern did not show any peak for impurity phases.

The characteristics of the band alignment of heterojunction is very important for the application of $\text{In}_2\text{Se}_3/\text{Si}$ heterojunction as photodetector. There are many situations for which energy band structure diagram can be simulated by using the Anderson–Shockley model. However, in this paper, experimental methods are used to study the energy band offset of the $\text{In}_2\text{Se}_3/\text{Si}$ heterojunction interface.

Fig. 2 shows $\text{Se}3\text{d}$ core level peak from the top In_2Se_3 layer and $\text{Si}2\text{p}$ core level peak originating from the underlying Si, and the difference in the core binding energy (ΔE_{CL}) for $\text{In}_2\text{Se}_3/\text{Si}$ heterojunction. The valence band maximum (VBM) was determined by using linear extrapolation. The valence band offset (ΔE_v) in terms of a binding energy difference ΔE_{CL} between core levels from each side of the interface is:

$$\Delta E_v = (E_{\text{Si}2\text{p}}^{\text{Si}} - E_{\text{VBM}}^{\text{Si}}) - (E_{\text{Se}3\text{d}}^{\text{In}_2\text{Se}_3} - E_{\text{VBM}}^{\text{In}_2\text{Se}_3}) - \Delta E_{\text{CL}} \quad (1)$$

$$\Delta E_{\text{CL}} = (E_{\text{Si}2\text{p}}^{\text{Si}} - E_{\text{Se}3\text{d}}^{\text{In}_2\text{Se}_3}). \quad (2)$$

The peak position of $\text{Si}2\text{p}$ -core level in Si and $\text{In}_2\text{Se}_3/\text{Si}$ found to be 98.98 ± 0.05 eV and 99.33 ± 0.05 eV, respectively (as shown in Fig. 2a). The CL of $\text{Se}3\text{d}$ in In_2Se_3 was at 54.34 ± 0.05 eV, and in $\text{In}_2\text{Se}_3/\text{Si}$ heterojunction at approximately 53.94 ± 0.05 eV (as shown in Fig. 2b). The valence band edge shown in Fig. 2c was used to measure the position of the VBM. The VBM of Si and

In_2Se_3 were determined to be 0.04 eV and 0.99 ± 0.1 eV, respectively. The Fig. 2c illustrates fitting of the low energy portion of the spectrum.

After the above data is substituted into eqn (1), the value of VBO (ΔE_v) is calculated to be 1.2 eV. Since $\gamma\text{-In}_2\text{Se}_3$ is a direct bandgap semiconductor, the band gap of In_2Se_3 can be extrapolated to 2.05 eV.³² This is consistent with the previously reported data that band gap of layered $\gamma\text{-In}_2\text{Se}_3$ lies at 2–2.5 eV.³⁷ As an indirect bandgap semiconductor, Si has a band gap of 1.12 eV at room temperature.

$$\Delta E_c = E_{\text{g}}^{\text{In}_2\text{Se}_3} - E_{\text{g}}^{\text{Si}} - \Delta E_v. \quad (3)$$

Therefore, the conduction band offset (CBO) value is calculated to be -0.27 eV by eqn (3). The energy band diagram of $\gamma\text{-In}_2\text{Se}_3/\text{Si}$ heterojunction is shown in Fig. 2d. Analyzing the band structure, it can be concluded that this heterojunction has a type II aligned structure.

The typical structure of $\gamma\text{-In}_2\text{Se}_3/\text{p-Si}$ heterojunction photodetector is shown in the inset of Fig. 3. Fig. 3 shows a typical current–voltage (I – V) characteristic of different metal–semiconductor contacts. The result shows that all the three contacts: $\text{Si-In}_2\text{Se}_3$, In-Si , $\text{Au-In}_2\text{Se}_3$ are Schottky contacts, the influence of contact between Au and In_2Se_3 and between In and Si can be neglected; the rectification behavior of this device mainly comes from the Schottky contact of the $\text{In}_2\text{Se}_3/\text{Si}$ heterojunction. And the rectification ratio is calculated 76 from the figure. Therefore, the $\gamma\text{-In}_2\text{Se}_3\text{-ML/Si}$ heterojunction appears to be a well-defined diode with a turn-on voltage of approximately 0.7 V.

Fig. 4a–d shows reverse biased portion of the I – V curve of $\gamma\text{-In}_2\text{Se}_3/\text{p-Si}$ heterojunction in the dark, and at different light intensities using LED point light sources of 365, 420, and 500 nm for illumination (IK3301R-G). The reverse bias characteristics

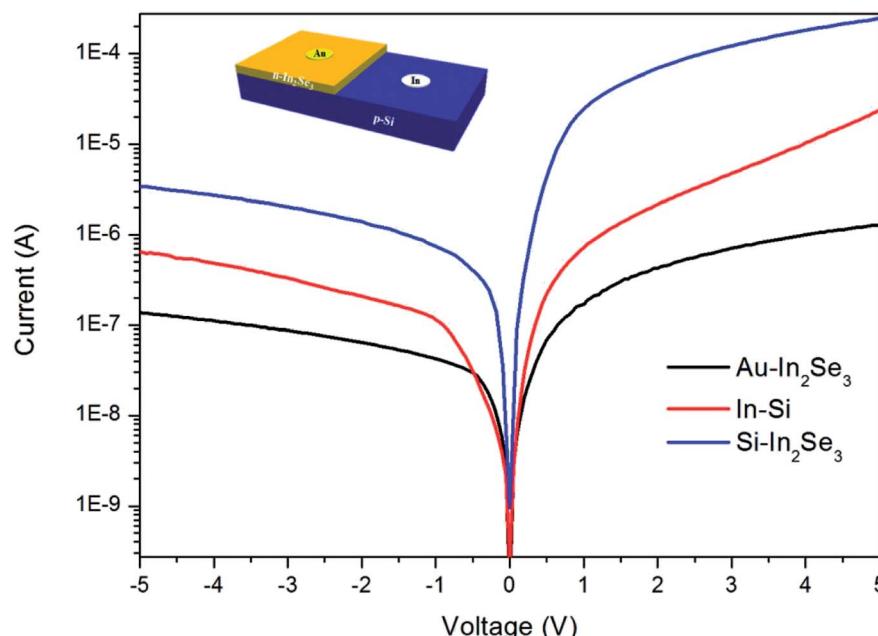


Fig. 3 A typical plots of current voltage characteristics in different metal–semiconductor contacts and $\text{In}_2\text{Se}_3/\text{Si}$ heterojunction. (Inset: schematic diagram of the $\gamma\text{-In}_2\text{Se}_3\text{-ML/Si}$ heterojunction photodetector).



also confirms the rectifying behavior of the γ -In₂Se₃-ML/Si heterojunction. During forward bias condition, the current increases exponentially with voltage, whereas at larger reverse voltages, the increase in current tends to saturate. The reverse biased IV characteristics of γ -In₂Se₃/Si heterojunction in the dark and presence of light also confirms its photodiode behavior. As shown by the reverse biased I - V curves, the dark current is about -0.98 nA. Under the illumination of the LED spot light source, a notable increase in the current in the reverse biased region was observed. With three different light sources, the photoresponse was tested at different light intensities and wavelengths. Fig. 4d shows the strong photoresponse dependence on light intensity. The photocurrent increases significantly with increase in light intensity. These characteristics demonstrate high photosensitivity of the device under ultraviolet to visible light irradiation.

Using the power law function to fit the three curves in Fig. 4d, it was found that there is almost a linear relationship between the photocurrent and optical power density. The power law function: $I_{\text{ph}} = AP^{\alpha}$, where I_{ph} stands for photocurrent ($I_{\text{illumination}} - I_{\text{dark}}$); A is a constant at a specific wavelength; P is the power density of the incident light; and α is a power law index. The fitted curves show that α is 0.96, 0.86 and 0.56 for wavelengths of 365, 420 and 500 nm, respectively.

Since the heterojunction is formed by two materials with different lattice constants and lattice structures, the energy band at the interface is discontinuous and there are potential barriers and potential wells. Different lattice constants introduce defects and interface states heterojunction interface. First of all, at 500 nm, α is only 0.56. This sub-linear response is a result of complex process of electron–hole generation, trapping, and recombination in the semiconductors. At wavelengths of light of 365 and 420 nm, the alpha factor is close to the ideal state one, particularly at 365 nm, which indicates that the losses caused by recombination in the process of photoexcitation of carriers are relatively low. Both the trap states in In₂Se₃ and at the interface between In₂Se₃ and Si substrates may have recombination centers, which has also been confirmed in other photodetector materials.^{37,38} It can also be seen from Fig. 4d that the photocurrent increases more slowly as the light intensity increases at a wavelength of 365 nm as compared to 420 nm incident light at the bias voltage of -5 V. In contrast, the photocurrent from 420 nm light intensity increases faster.

The responsivity (R_{res}) is a useful figure-of-merit for a photodetector, which can be calculated from:

$$R_{\text{res}} = I_{\text{ph}}/I_{\text{irr}}A \quad (4)$$

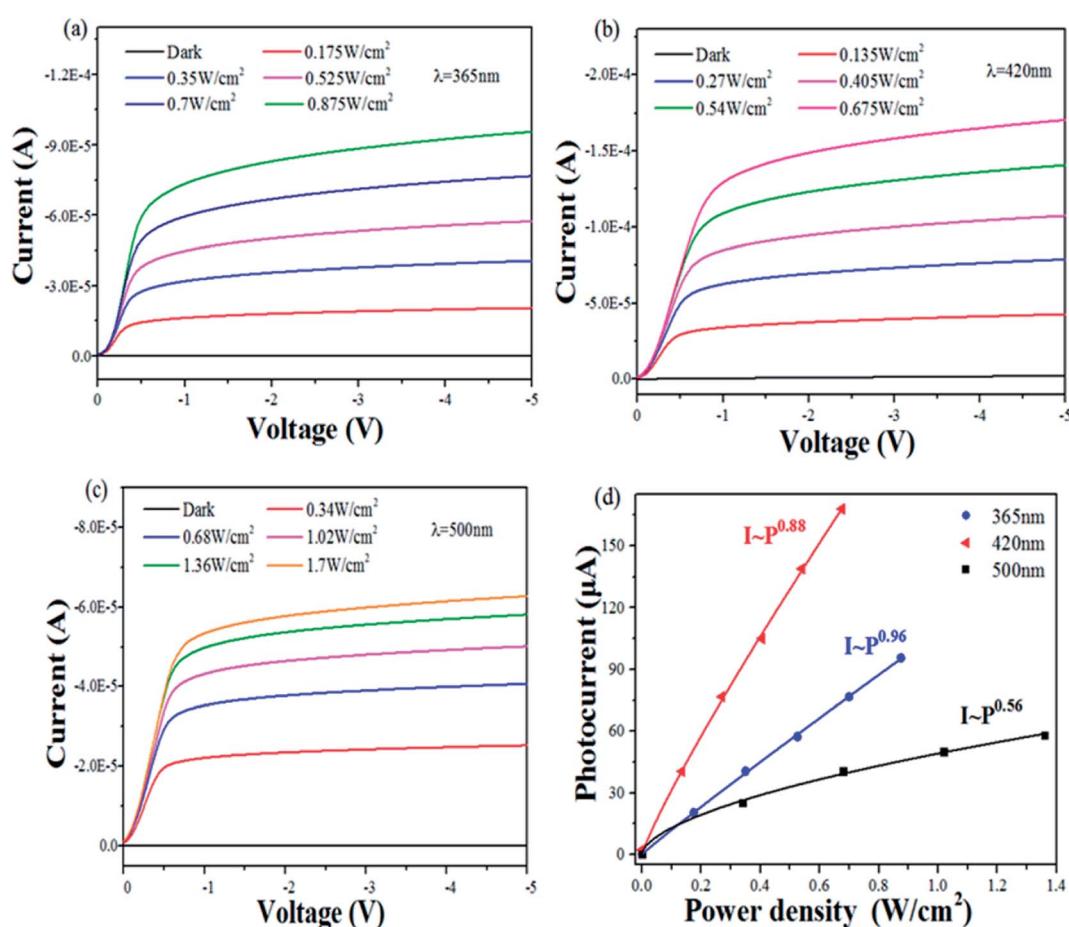


Fig. 4 Photoelectric characteristics of In₂Se₃-ML/Si heterojunction in the dark, and their photoresponse at various wavelengths and different illumination intensities: (a) 360, (b) 420, and (c) 500 nm and; (d) photocurrent as a function of light intensity under the reverse bias voltage of -5 V.

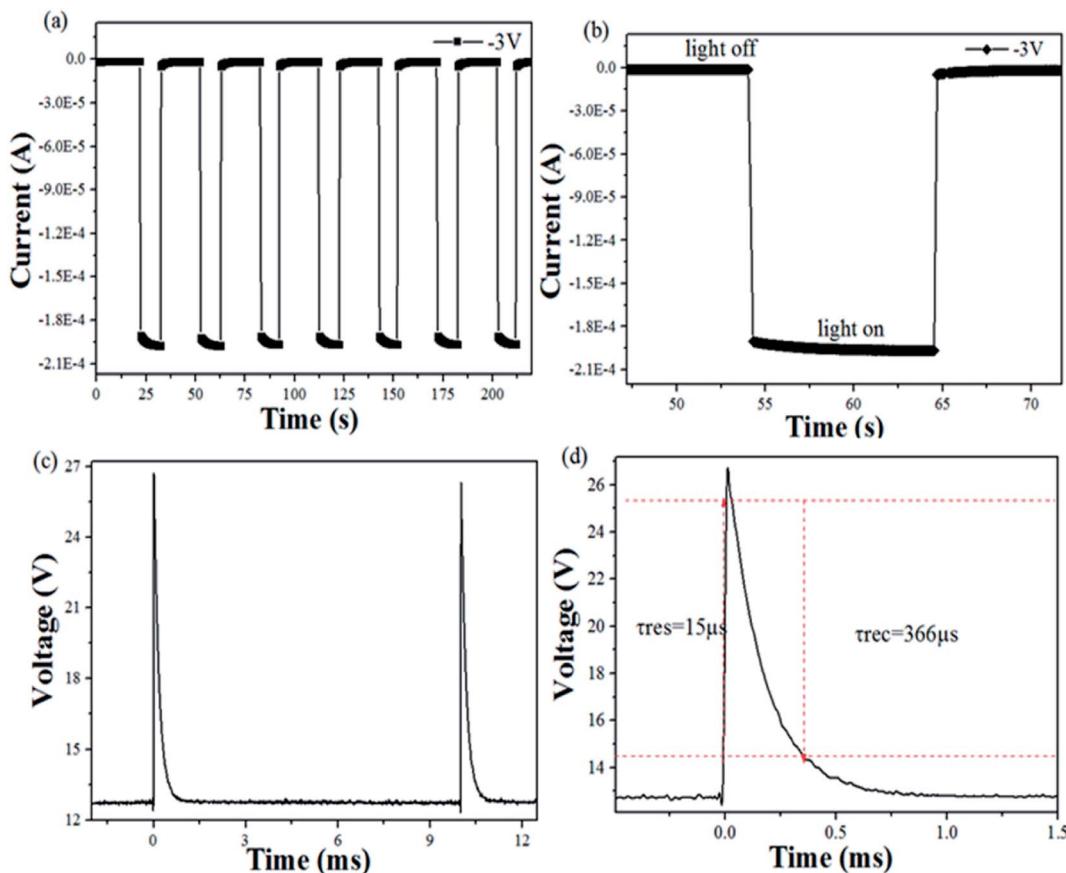


Fig. 5 Optoelectronic performance of In_2Se_3 -ML/Si heterojunction: (a) the seven-cycle time-resolved photoresponse under a bias of -3 V at 365 nm light illumination, (b) a single-period plot of the time-resolved photoresponse, (c) photoresponse of the photodetector at 266 nm laser by a Q-switch Nd:YAG and (d) photoresponse of single period in (c).

where I_{ph} is the photocurrent, I_{irr} is the irradiance of the incident light, and A is the effective illuminated area ($2 \times 10^{-4} \text{ cm}^2$ for this device).³⁹ According to photoresponse at 365 nm of 0.175 W cm^{-2} , as shown in Fig. 4, the optical responsivity is calculated 0.54 AW^{-1} , which is higher than other nanomaterials.^{7,40}

The other important figure-of-merit is the external quantum efficiency (η), which can be calculated from:

$$\eta = (I_{\text{ph}}/e)/(I_{\text{irr}}A/h\nu) \quad (5)$$

where e is the elementary charge, h is the Planck constant, and ν is the electromagnetic frequency. The external quantum efficiency is calculated 1.84 , which exhibit excellent performance.

The detectivity (D) can be calculated from:

$$D = R_{\text{res}}/(2qJ_{\text{d}})^{1/2} \quad (6)$$

where q is the fundamental unit of charge, J_{d} is the dark current.³⁹ And D is calculated 3.53×10^{12} , which is higher than other nanomaterials.^{7,40}

A time-resolved photo-response diagram under illumination of 365 nm light source with a reverse bias of -3 V is shown in Fig. 5a. Under the bias of -3 V, the current increases significantly from $-1.5 \mu \text{A}$ (light off) to $-192 \mu \text{A}$ (light on). Switch "on/"

off" ratio was found up to 128 . The consistency of the seven switching cycles in Fig. 5a shows that the optical response has good stability and repeatability.

Fig. 5c shows typical time response characteristics of γ - In_2Se_3 /p-Si heterojunction photodiode. The response speed of the photodetector is usually characterized by the response time (τ_{res}) and the recovery time τ_{rec} . Whereas, response time is defined as the time required to increase 10% of its peak value to 90% , and the recovery time is the time taken to decay from 90% to 10% of its peak value. In order to extract an accurate response time, an enlarged response cycle is shown in Fig. 5d. The short response time ($15 \mu \text{s}$) and recovery time ($366 \mu \text{s}$) were observed in this work, which are much smaller than other heterojunction (such as α - In_2Se_3 ($6 \text{ ms}/12 \text{ ms}$), γ - In_2Se_3 ($175 \mu \text{s}/226 \mu \text{s}$), ZnO (10^4 /-), MoS_2 ($31 \mu \text{s}/72 \mu \text{s}$)).^{26,39,41,42} The ultrafast response attributed to II structure band alignment was good at the separation of electrons-hole pairs, and can fastly reduce their recombination.

3 Conclusions

In this paper, high quality γ - In_2Se_3 /p-Si heterojunction were prepared using PLD. The band alignment of In_2Se_3 /Si heterojunction was measured by XPS. The valence band offset (ΔE_v) and the conduction band offset (ΔE_c) of the heterojunction were



determined to be 1.2 ± 0.1 eV and 0.27 ± 0.1 eV, respectively. Analysis of the band structure indicates that the γ -In₂Se₃/p-Si heterojunction has a type II band alignment structure. The γ -In₂Se₃/p-Si heterojunction photodiodes exhibit excellent rectification characteristics in the dark and at different incident optical powers, and have a broad spectral response ranging from UV to VIS with high responsivity and stability. And the ultrafast response time (15 μ s) and recovery time (366 μ s) indicate that the heterojunction has a fast response and detection performance.

Conflicts of interest

There are no conflicts to declare.

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