Ultrafast and broadband photodetection based on selenized AgSbS₂ thin films prepared by spray pyrolysis deposition and modified with indium nitrate†

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Silver antimony sulfide (AgSbS₂) stands out as a promising absorber material for optoelectronic devices, thanks to its exceptional optical properties, solution processability, and versatile composition tunability. However, its practical application in long-wave photodetection is hindered by the relatively large band gap (~1.7 eV). While selenization can reduce the band gap, its effectiveness is often limited by the compact crystal grain structure, especially in thick films, leading to an insufficient selenization rate. Consequently, photodetectors based on selenized AgSbS₂ exhibit minimal response to infrared radiation. To address this challenge, we propose a novel approach: constructing a porous AgSbS₂ precursor by incorporating higher solubility indium nitrate into the spray solution. We have developed a model that considers the crystallization aspect to explain the formation of this porous morphology and crystal structure. The resulting AgSbS₂(Se) photodetectors exhibit a broadband response range extending beyond 1920 nm and a high bandwidth of up to 0.3 MHz, owing to the special gradient structure with a high selenization rate. These outstanding features suggest great potential for application in high-speed photon computation and communication systems. Moreover, it opens up new possibilities for developing high-performance broadband photodetectors by reconstructing existing compound semiconductors.

1 Introduction

Heterojunction infrared photodetectors (PDs) with excellent spectral selectivity and rapid responsiveness play a crucial role in modern optoelectronics, finding applications in various fields such as photon computation/communication, autonomous vehicles, and medical equipment.1,2 The demand for broadband photodetection covering the 1300–1550 nm wavelength range has gained significant importance for long-distance and low-loss optical fiber data transmission. Photonic devices operating within this range can be directly connected to external servers without the need for wavelength conversion, leading to streamlined communication.3 To meet the stringent “6S” criteria for photoelectric devices,4 high response speed and responsivity are essential to ensure a high signal transmission rate and fidelity.

In pursuit of broadband photodetection, narrow-bandgap semiconductors such as InGaAs5 and HgCdTe6 have been extensively employed in both laboratory and commercial infrared PD fabrication. However, their complex preparation processes, high costs, low linear dynamic range, and low-temperature operating conditions have restricted their widespread adoption. Recently, two-dimensional (2D) materials, including MoS₂, PdSe₂, Si₂Te₃, and graphene, have garnered attention for their wide response spectrum (~1700 nm).7–9 Although these materials hold promise for applications in flexible electronics, their use in photon communication is limited by unstable factors arising from the weak van der Waals bonding in heterojunction interfaces.10,11 These photodetectors are not very stable, especially in large current situations due to the sharp interface. They also usually show poor chemical stability and sensitivity to moisture and oxygen.12 Nanocrystalline detectors based on ternary antimony disulfide (including CuSbS₂ and AgSbS₂) prepared on a silicon substrate usually

† Electronic supplementary information (ESI) available: Preparation of AgSbS₂ thin films by spray pyrolysis. Infrared photodetectors were fabricated with an ITO/CdS/AgSbS₂(Se)/Au structure. See DOI: https://doi.org/10.1039/d3ta06426c
exhibit A/W-level responsibility with very high detectivity, attributed to the good photodiode behavior and a high rectifying ratio.\textsuperscript{13,14} Nonetheless, the performance is always constrained by the synthesis technology of narrow-bandgap nanocrystals, as well as the stability of nanomaterials. Conjugated polymer infrared PDs have also demonstrated a relatively wide detection range up to 1500 nm, high detectivity exceeding 10\textsuperscript{10} Jones, and micrometer-scale response times. However, the issue of aging must be addressed before their engineering application.\textsuperscript{15,16}

Thin film PDs based on binary metal chalcogenides, such as In\textsubscript{2}Se\textsubscript{3}, SnSe\textsubscript{2}, Sb\textsubscript{2}Se\textsubscript{3}, and CdSe,\textsuperscript{17–21} have shown weak response in the long-wave infrared range, with most research focused on the visible to short-wave infrared region (<1100 nm).\textsuperscript{22} Consequently, achieving high response speed and high responsivity photodetection in the long-wave infrared range remains a persistent challenge.

Recently, miargyrite silver antimony chalcogenides AgSbS\textsubscript{2} and AgSbSe\textsubscript{2} have garnered significant attention due to their exceptional photovoltaic properties, including a high absorption coefficient (10\textsuperscript{4}–10\textsuperscript{6} cm\textsuperscript{-1}) ranging from ultraviolet (UV) to near-infrared (NIR), an appropriate bandgap, and excellent chemical stability.\textsuperscript{23–26} Their environmental friendliness and abundant composition makes them suitable absorbers for next-generation solar cells. Furthermore, their low dark current, fast carrier transport, and tunable bandgap offer promising prospects for ultrafast and broadband photodetection.\textsuperscript{27–30} While single-phase AgSbS\textsubscript{2} thin films can be easily prepared via solution methods such as spin-coating and spray pyrolysis, their large band gap (direct and indirect band gaps are 1.64 eV and 1.49 eV, respectively) results in weak responses in the long-wave range (>900 nm).\textsuperscript{31–33} On the other hand, AgSbSe\textsubscript{2} with a lower direct band gap (1.0–1.1 eV) exhibits a much broader detection range.\textsuperscript{33} AgSbSe\textsubscript{2} has a significantly narrow indirect band gap of about 0.58–0.64 eV, indicating that the photodetectors could have a possibility to detect longer wavelength infrared radiation up to 2 μm. However, the preparation of AgSbSe\textsubscript{2} thin films poses challenges, as there is a scarcity of soluble Se sources that can release Se\textsuperscript{2} without introducing second-phase materials. Vacuum deposition methods including thermal evaporation and magnetron sputtering often yield poor stoichiometric control, as the selenium element easily escapes from the body. Another method is to selenize the precursor, e.g., by heating stacked layers of Sb\textsubscript{2}Se\textsubscript{3}/Se/Ag.\textsuperscript{34} Unfortunately, it is difficult to find a heating temperature high enough to realize a single phase while there is not much selenium loss. Furthermore, the film could only be designed to be very thin (~200 nm); otherwise, it will detach from the substrate due to the stress caused by Se atoms entering the lattice. Obviously, the photovoltaic performance of the device prepared by this method is not optimal. To date, the understanding of AgSbS\textsubscript{2} and AgSbSe\textsubscript{2} photoelectric performance is still inadequate.

In this study, we prepared AgSbS\textsubscript{2} films via a spray pyrolysis method, and through a selenidation process, a portion of S atoms in the AgSbS\textsubscript{2} film was substituted by Se, resulting in a reduction in the band gap. Infrared photodetectors were fabricated with an ITO/Cds/AgSbS\textsubscript{2}(Se)/Ag structure. To optimize the selenidation level, indium nitrate was introduced. The devices exhibited high response speed and responsivity across a broad range up to 1920 nm. The photodetectors displayed a remarkable responsivity of 5.57 mA W\textsuperscript{-1} and a detectivity of 7.43 × 10\textsuperscript{9} Jones at 1550 nm. With rise and decay times of 1.12 μs and 0.75 μs, respectively, these photodetectors hold significant promise for high-speed photon computation and communication applications.

2 Results and discussion

The AgSbS\textsubscript{2} thin films were prepared via the spray pyrolysis method, using a 2-methoxyethanol solution containing silver nitrate, antimony acetate, and thiourea, as previously reported.\textsuperscript{35} Subsequently, a post-selenidation process was employed to promote the substitution of S atoms with Se in the AgSbS\textsubscript{2} film, as illustrated in Fig. 1a. To evaluate the photodetection capability, photodetectors with an ITO/Cds/AgSbS\textsubscript{2}(Se)/Au structure were utilized, wherein ITO glass serves as the transparent conductive electrode, Cds acts as an n-type window layer, and AgSbS\textsubscript{2}(Se) functions as a p-type absorber. Photocarriers are generated and separated by the Cds/AgSbS\textsubscript{2}(Se) interface, while Au, being a high work function metal, extracts and collects hole carriers. The device structure and energy levels are shown schematically in Fig. 1b and c, respectively.

According to Fick’s second law, a gradient composition distribution would form in the selenized film, where the surface is highly selenized AgSbS\textsubscript{2} (HS-AgSbS\textsubscript{2}(Se)), and the composition near the p–n junction is less selenized AgSbS\textsubscript{2} (LS-AgSbS\textsubscript{2}(Se)). This results in a cascaded band alignment (Fig. 1c), significantly increasing the efficiency of electron and hole extraction. Meanwhile, HS-AgSbS\textsubscript{2}(Se) on the rear side allows for the absorption of low-energy photons, leading to spectral enhancement at longer wavelengths. To optimize the film’s morphology and band structure, a substantial amount of indium nitrate was introduced into the spray solution. As revealed in Fig. 2a, a photograph of the untreated film, along with films after vacuum annealing and selenidation, was captured under backlight. The as-prepared sample exhibited a brown translucent appearance, while after annealing, its transparency significantly improved. The unselezined films changed to a black color with a gleaming metallic luster, indicating compositional changes and a reduction in the band gap.

Top-view scanning electron microscopy (SEM) images of films without indium before and after selenidation are presented in Fig. 2b and c, respectively. The untreated film without indium showed clear crystal grains and a compact crystaline texture, which could hinder Se distribution from the surface to the body of the films during the selenidation process, resulting in a low selenidation rate. In contrast, the film in Fig. 2d, modified with indium nitrate, exhibited a looser appearance with porous nanostructures. The underdeveloped quasi-crystal grains close to indium-free films can be distinguished, revealing a considerable space with a width of about 10–50 nm between adjoining quasi-crystal grains. After the post-selenidation process, the surface of the film without indium showed a small change, with a visible improvement in compactness and crystallinity,\textsuperscript{36} as depicted in Fig. 2c. In
contrast, the film with indium showed significant structural changes after selenidation. Fig. 2e shows an image of the selenized film with an In/Sb ratio of 0.5. As we can see, the cracks and spaces completely disappeared, and the film exhibited an optimal compact structure with very few pinholes. A cross-sectional view of the films further confirmed this observation, as shown in Fig. 2f–i. Untreated films without indium exhibited a clear distinction from the CdS and ITO substrate (Fig. 2f). After selenidation, crystal grains with sizes ranging from 80 to 100 nm were observed, indicating a higher degree of crystallinity compared to that of untreated samples, as shown in Fig. 2g. In contrast, the untreated film with indium depicted in Fig. 2h exhibited a much looser amorphous-like cross-section with some indistinct small particles. After selenidation, the average size with indium was about 40–50 nm, indicating that adding indium nitrate to the spray solution could facilitate sufficient selenization and bring about a grain refinement effect.

The influence of indium on the film’s crystallization process during spray pyrolysis was analyzed. As depicted in Fig. 3a, the evolution of the spray solution during the pyrolysis process indicated that nucleation could occur in the absence of indium due to the low reaction energy barrier for Ag⁺ and Sb³⁺ reacting with S²⁻. Subsequently, crystal domains grew larger by absorbing solutes from the spray solution. However, indium-containing components separated out last from the solution, resulting in a significant amount of space between the quasi-grains. This interval space was crucial for the selenidation rate. As a result, the selenidation depth and rate of films modified with indium nitrate were significantly higher than those of films without indium, as illustrated in Fig. 3b.

X-ray diffraction (XRD) was used to examine the crystal structure variation due to indium modification during the selenidation process. The XRD patterns of films with and without indium, treated by vacuum annealing and selenization, are presented in Fig. 3c. Vacuum annealed films showed low crystallinity and diffraction intensity. The XRD spectra of selenized samples closely resembled the AgSbS₂ and AgSbSe₂ standard cards (JCPDS No. 17-0456 and 12-0379) with a slight consistent diffraction peak shift, indicating partial substitution of S with Se during the selenidation process. Notably, there is no significant structure change for both AgSbS₂ and AgSbS₂(Se) films even when a large amount of indium nitrate (In : Sb = 0.5) was added. The films still retained a miargyrite crystal structure even without significant changes in peak intensity.

For the vacuum annealed samples, the XRD peaks of the film with indium consistently shifted to larger 2θ compared to that of the film without indium. This shift could be caused by the substitution of antimony by indium with lattice contraction. The selenized sample with indium shows much lower second-phase XRD peaks than that without indium, indicating that the addition of indium inhibited the formation of Sb-enriched impurities. The magnified (200) diffraction peaks of the selenized samples in Fig. 3d revealed that the sample with indium displayed an obviously smaller 2θ and broader full width at half maximum (FWHM) than the sample without indium. The
Diffraction peaks shift by a small angle could be caused by the selenium substitution, because the ion ratio of $\text{Se}^{2-}$ is much higher than that of $\text{S}^{2-}$. Each (200) peak for the two samples is between AgSbS$_2$ and AgSbSe$_2$ standard peaks, implying that the S substitution by Se of the films is partial. The XRD spectrum of the selenized sample with indium is very close to that of AgSbSe$_2$ standard PDF (12-0379), indicating the large amount of S substitution by Se.

The elemental analysis of films was conducted by energy-dispersive spectroscopy (EDS). Fig. 3e shows the Se/S ratio varied with different indium concentrations. EDS spectra and the detailed atomic percentage for the S, Se, Ag, Sb, and In elements are shown in Fig. S1–S5 and Table S1. The Se concentration in films gradually increased with increasing In/Sb ratio from 0.3 to 0.5 for the same selenidation time. For the film without indium selenized for 10 min, the ratio of Se/(S + Se) is 32.32%, showing that 32.32% S has been substituted by Se. When indium was added, for example, In/Sb ratio = 0.5, and the substitution rate of films was largely increased to 77.01%. However, an excessive amount of indium (In/Sb = 1) led to a decreased selenidation rate. Overall, the sample with an In/Sb ratio of 0.5 exhibited the best selenidation rate. These pieces of evidence suggest that the selenidation rate could be significantly improved by the introduction of indium.

High-resolution transmission electron microscope (HRTEM) images with the lattice fringes of the selenized samples without and with indium are shown in Fig. 3f and g. The interplanar spacing of (111) and (110) is 0.330 nm and 0.202 nm for the indium-free sample. When indium was added, the interplanar spacing of (111) and (110) increased to 0.336 nm and 0.208 nm. Accordingly, the selected area electron diffraction (SAED) patterns show that all of the diffraction rings for samples with indium slightly decreased, indicating the expansion of the crystal lattice, the tendency of which is agrees well with the XRD results. From the XRD results, it is difficult to find any obvious XRD peaks related to indium compounds, even when a large amount of indium nitrate (In : Sb = 0.5) was added. As we discussed in the crystallization process during spray pyrolysis (Fig. 3a), indium-containing components are more likely to exist in the space of crystal grains in an amorphous state. Although the component analysis has many uncertainties, the effect of...
indium on the film organization and selenization rate is quite clear.

X-ray photoelectron spectroscopy (XPS) measurements were utilized to investigate the chemical state of the film’s surface. The XPS survey of selenized films with and without indium displayed similar peak intensities for elements (Fig. 4a). The In 3d XPS peak of the film with indium was easily discernible in both the survey and high-resolution spectra (Fig. 4b). The Ag 3d XPS peaks exhibited negligible differences in binding energy and intensity between the two samples, indicating that the presence of indium had little effect on the chemical state of Ag, as shown in Fig. 4c. The Sb 3d XPS peaks in Fig. 4d consistently shifted to a higher binding energy (from 538.16 to 538.45 eV for Sb 3d_{3/2} and from 528.84 to 529.04 eV for Sb 3d_{5/2}) compared to those of the sample without indium. This chemical shift may overlap with the relative position shift of the Fermi level in the surface band gap ($\Delta E_F = E_F - E_V$), possibly related to the enhancement of the selenidation level. This confirms that the addition of indium nitrate has improved the selenization rate and also brought an increase in Se content in the surface. Fig. 4e and f show the Se 3d XPS peaks and S 2p XPS peaks for the films with and without indium. For both samples, S 2p...
signals were detected, implying that only a portion of Se had been substituted, even at the film's surface, as XPS could not detect signals at a depth of more than 5 nm in inorganic samples. As in the previous study, the S 2p XPS peaks would shift to a lower binding energy when the selenium content increases in antimony sulfides. However, Sb 2p3/2 and Sb 2p5/2 here shifted to higher binding energy from 165.49 to 165.84 eV and from 159.85 to 160.04 eV, respectively. This anomaly could be related to the substitution of Sb by the In element.

Upon conducting the aforementioned measurements, we deduce that Se diffusion was constrained by the grain boundaries, limiting the selenidation process primarily to the film's surface and the grain interfaces, particularly for shorter selenidation periods. The addition of indium nitrate played a crucial role in reorganizing the grain structure and creating a more loosely packed film, thus facilitating Se transport from the surface to the body of the film and generating a vertical gradient of Se distribution.

Fig. 5a shows the dark-field imaging (HAADF)-scanning transmission electron microscope (STEM) and EDS mapping images for the cross-section of an AgSbS2(Se) film modified with indium. As seen, the intense Se element signal is much higher than that of S, agreeing well with the EDS results in Fig. 3e. The Se element exhibits a gradient distribution that is enriched in the near surface and depleted near the p–n junction interface. The S element shows an opposite distribution, with most of it remaining near the p–n junction. Interestingly, the EDS signals of the In element have the opposite contrast with that of the Sb element, showing that much indium got into the crystal lattice, and most of the indium was distributed in the space between AgSbS2 crystal grains, which agrees well with the XRD results.

The ultraviolet-visible-near-infrared (UV-vis-NIR) spectrum of films selenized for different times with varying Se/S ratios is displayed in Fig. S6.† As the In/Sb ratio increased from 0 to 0.5, the film’s absorption and absorption edge shifted from 720 nm to 1000 nm, indicating that the film modified with indium nitrate exhibited enhanced detectability for longer infrared wavelengths. To determine the average energy band gap ($E_g$) of the films, we employed a linear fitting of the $(a h \nu)^2 - h \nu$ curve, where $a$ is the absorption coefficient, $h$ is the Planck constant, and $\nu$ is the frequency of the incident photons. The results, shown in Fig. 5b, revealed a gradual decrease in the nominal $E_g$ from 1.61 to 1.32 eV as the In/Sb content ratio increased from 0 to 0.5. While precisely determining the accurate energy levels in this inhomogeneous film presented challenges, a figurative schematic was constructed to illustrate the photoelectric process in AgSbS2(Se) films. Fig. 5c depicts the schematic energy level of the CdS/AgSbS2(Se) device, which could be simulated using an active diffusion model with Fick's second law, as detailed in our previously reported work. The film exhibited a gradient composition distribution with a gradient band structure from the top surface to the body, where the $E_g$ near the top surface was very close to that of AgSbSe2 (1.0 eV). Near the heterojunction interface, the composition was primarily unselenized AgSbS2 with a broad $E_g$ of 1.7 eV. This structural design was advantageous for achieving broad light absorption and maintaining a high built-in electric field ($V_{bi}$) to reduce carrier recombination.
The addition of indium nitrate significantly improved the selenization rate. The higher Se concentration not only improves the absorption range and intensity, but also enhances the carrier transport properties of the AgSbS2(Se) film. To investigate the charge recombination behavior of the CdS/AgSbS2(Se) device, we conducted electrochemical impedance spectroscopy (EIS) on devices with and without indium. Fig. 5d displays the EIS spectra and the corresponding equivalent circuit model, enabling an analysis of the charge recombination behavior through the fitting of series resistance ($R_s$), interfacial recombination resistance ($R_{\text{rec}}$), and capacitance ($C_{\text{rec}}$) in the equivalent circuit. The low-frequency region in the EIS spectrum directly reflected the interfacial charge recombination process. The device without indium exhibited $R_s$ and $R_{\text{rec}}$ values of 33.05 and 58.16 Ω, respectively. However, with the addition of indium nitrate to the spray solution, the device demonstrated a much higher $R_{\text{rec}}$ of 140.20 Ω and a decreased $R_s$ of 27.20 Ω, indicating a remarkable inhibition of charge recombination centers and providing a more efficient carrier transport path. Due to the significant differences in absorption conditions, the built-in electric field and carrier transport properties, the devices without and with indium show different photovoltaic performances. Fig. 5e shows the photocurrent–voltage characteristics for the device without indium, with an In/Sb ratio of 0.2 and 0.5. The device without indium shows a high open-circuit voltage ($V_{\text{OC}}$) of 0.37 V and a low short-circuit current ($I_{\text{SC}}$) of 0.28 mA under AM 1.5G illumination with a power intensity of 100 mW cm$^{-2}$. When the In/Sb ratio is 0.2, the $V_{\text{OC}}$ decreased to 0.23 V with increasing $I_{\text{SC}}$ to 0.50 mA. For the device with an In/Sb ratio of 0.5, due to the narrow bandgap, the $I_{\text{SC}}$ reached 0.81 mA, which is nearly 3 times higher than that of the indium-free device. The extremely high photocurrent represents its good performance as a self-powered photodetector.

To investigate the optoelectronic properties of the AgSbS2(Se) absorber modified with indium nitrate, photodetectors with a structure similar to that in Fig. 1b and an active area of 0.04 cm$^2$ were fabricated. Fig. 6a illustrates a comparison of the current–time ($I$–$T$) characteristics between the devices with and without indium, while Fig. 6b and c show their respective individual photo responses. The AgSbS2 photodetector without indium exhibited low photo response only in the shortwave range (∼660 nm) due to its broad bandgap and low absorption in the long wavelength range. A photocurrent response to 660 nm light for the device without indium is shown in Fig. S7.† As seen in Fig. 6b, the photocurrent sharply decreased from 14.6 to 0.5 μA when the light source was switched from 660 to 760 nm at a power density of 10 mW cm$^{-2}$. Additionally, the photocurrent gradually decreased as the wavelength increased, as observed at equal light intensity. In comparison, the device based on the AgSbS2(Se) film with an In/Sb ratio of 0.5 demonstrated a 1–3 orders of magnitude
higher photo response within the test range. The photocurrent reached 0.45 mA when illuminated with 660 nm light at a power density of 10 mW cm\(^{-2}\). Even under 1050 nm illumination, the photocurrent remained as high as 53 \(\mu\)A, as shown in Fig. 6c.

To further assess the performance of the photodetector, the light responsivity \((R, \text{W}^{-1})\) was calculated using the following formula:

\[
R = \frac{I_{\text{light}} - I_{\text{dark}}}{P \times A}
\]

(1)

The external quantum efficiency (EQE) represents the efficiency of the device in converting incident photons into electrons, which could be calculated using the following formula:

\[
\text{EQE} = \frac{hc}{e \lambda R}
\]

(2)

here \(I_{\text{light}}\) and \(I_{\text{dark}}\) represent photocurrent and dark current, respectively. \(P\) is the power density of light, \(A\) is the area of light, \(h\) is the Planck constant, \(c\) is the speed of light in a vacuum, \(e\) is the absolute value of the electronic charge, and \(\lambda\) is the wavelength of the incident light. A comparison of the parameters at different wavelengths for the photodetectors with and without indium is shown in Fig. S8.† The photodetector with indium shows a significantly higher and broader EQE (Fig. 6d) than that without indium in all test ranges. The maximum EQE value is 76.4–77.8%, occurring at 660–760 nm. Under 1050 nm illumination, the EQE value remains high at 10%. Even at 1550 nm, the EQE value remains higher than 1%. In contrast, the photodetector without indium exhibits a narrow photoresponse only in the visible range. The maximum EQE value is 46.1–51.2%, occurring at 460–500 nm. This detector has almost no response to infrared radiation. As the wavelength increases beyond 760 nm, the EQE value approaches 0. The variation in EQE directly illustrates the greatly improved detection ability of the device in all test ranges, especially in the long wavelength range, achieved by adding indium to the AgSbS\(_2\)(Se) absorber.

Fig. 6e presents the current–voltage (\(I\–V\)) characteristics of the indium-modified device under dark and 1050 nm infrared irradiation. The photocurrent at reverse bias voltage increases...
evenly as the power density increases from 10 to 50 mW cm\(^{-2}\). Fig. S9\(^\dagger\) shows the resistance calculated from I–V characteristics for the indium-modified device in the dark. As we can see, the device exhibits a resistance higher than 1000 \(\Omega\) only when the reverse bias voltage is below 0.25 V, indicating that the device is slightly leaking. The leakage here could be related to the narrow bandgap (with a direct bandgap of 1.1 eV and an indirect bandgap of 0.6 eV). Fortunately, they can be used as self-powered devices, and their background current could still be very small. The device photocurrent response to different power intensities of incident light shows typical characteristics of photodiodes, that is, the photocurrent is directly proportional to the intensity of incident light. Fig. S10\(^\dagger\) shows the photo response under 1050 nm irradiation with the power density ranging from 1 to 30 mW cm\(^{-2}\). The photocurrent here could be described as:

\[
I_{ph} = \eta \times P_{in} \times q \omega \tag{3}
\]

Here the term \(\eta\) denotes the gain coefficient, \(P_{in}\) represents the intensity of incident light, and \(q\) signifies elementary charge. Taking the responsivity of 1050 nm light as an example, the value of photocurrent \(I_{ph}\) can be expressed as a function of incident light intensity by fitting it with a simple linear relationship of \(I_{ph} = 0.00492P_{in}\). The device also demonstrates outstanding performance in response to ultra-weak infrared irradiation, as depicted in Fig. S11.\(^\dagger\) The current–time (I–T) curves exhibit clear on–off boundaries with low response times. The 40 nA photocurrent at 0.01 mW cm\(^{-2}\) power density underscores its excellent photodetector performance under low light intensity conditions. Fig. 6g illustrates the responsivity and detectivity \(D^*\) of the device measured under 1050 nm irradiation at various light intensities. Detectivity \(D^*\) represents the lowest level of light that the device can detect and can be calculated using the following equation:\(^{45}\)

\[
D^* = \frac{R}{\sqrt{2eI_{dark}/A}} \tag{4}
\]

The detectivity of our photodetector at 1050 nm was approximately 1.48–1.84 \times 10\(^{11}\) Jones, significantly surpassing that of many reported photodetectors. The detection limit is determined by the noise-equivalent-power (NEP), commonly defined as the signal power required to achieve a unity signal-to-noise ratio in the presence of a known (detector or background) noise.\(^{46}\) The NEP value can be derived using the following equation:

\[
\text{NEP} = \frac{i_n}{R_i} = \frac{\sqrt{2qI\Delta f}}{R_i} \tag{5}
\]

where \(I\) is the measured noise and \(\Delta f\) is the electrical bandwidth. The device with indium exhibits a very small NEP ranging from 2.39 \times 10\(^{-13}\) W Hz\(^{-0.5}\) to 1.61 \times 10\(^{-8}\) W Hz\(^{-0.5}\) across the entire response range, which is significantly lower than that of the device without indium. To assess the stability and lifetime of the photodetector, we measured the temporal response of the detector under ambient conditions by repeatedly switching the incident infrared light on/off every 10 s, as shown in Fig. 6i. As observed, the current on/off switching behavior remains robust, demonstrating that the device can achieve fast and stable switching with the infrared light on and off. Importantly, there is little deviation after 500 cycles, and the photocurrent difference is less than 10\(^{-3}\) without considering light attenuation, indicating the high stability of the photodetector.

To investigate the response at the energy band edge and the detectable range limit, we examined the photoresponse characteristics of the device under 1550 nm and 1920 nm lasers, as illustrated in Fig. 7a–f. Even at a weak intensity of 0.05 mW cm\(^{-2}\) from the two monochromatic lights, the device displayed a clear on/off state with an on/off ratio of 600, showcasing its high sensitivity to long-wave infrared light. As depicted in Fig. 7b, c, e and f, the values of \(I_{light}, R,\) and \(D^*\) are highly dependent on light intensity, exhibiting a linear dynamic range with a significant increase in light intensity.

Under 10 mW cm\(^{-2}\) irradiation at 1550 nm, the device exhibited an \(I_{light}\) of 2.23 \(\mu\)A, an \(R\) of 5.57 mA W\(^{-1}\), and a \(D^*\) of 7.43 \times 10\(^9\) Jones, accompanied by an EQE of 0.15%. Under 1920 nm irradiation, the device demonstrated an \(R\) value of approximately 0.20 mA W\(^{-1}\) and a \(D^*\) of 2.66 \times 10\(^9\) Jones under 10 mW cm\(^{-2}\) irradiation. These results indicate that the photodetector is capable of broadband photodetection across the 1300–1550 nm wavelength range, meeting the requirements for optimal wavelength coverage in laser communication.

The response speed is a crucial parameter that reflects the device’s ability to track rapid changes of light signals. To assess this ability, we utilized high-frequency pulses generated by a 980 nm semiconductor laser tube powered by a signal generator as a light source. Fig. 8a–d depict the optical response of the detector to pulsed light at different modulation frequencies ranging from 100 Hz to 0.8 MHz. The photocurrent was normalized based on the highest value. Our photodetectors exhibited excellent stability and repeatability across a broad frequency range up to 0.1 MHz. Even at a high frequency of 0.11–1 MHz, the device still displayed significant low and high photovoltage states, albeit with a decrease in optical response.

The relationship between the relative balance of light response \((V_{max} - V_{min})/V_{max}\) and modulation frequency for our device, along with a commercial Ge detector (GP3 GM6VHS), is further summarized and plotted in Fig. 5e. The response of the Ge detector to pulsed light at different modulation frequencies ranging from 100 Hz to 0.3 MHz is presented in Fig. S12a–e.\(^\dagger\) The results indicate that the relative balance value exhibits a slow decay trend as the switching frequency increases. In contrast, our device boasts a high 3 dB bandwidth of 0.27 MHz, significantly surpassing that of the commercial Ge detector (0.07 MHz). At an elevated frequency of 0.8 MHz, the relative balance value decreases by about 80%. The response time was calculated by recording the amplified light response curve at 0.1 MHz. As depicted in Fig. 8f, the rise and decay times of the device are 1.12 \(\mu\)s and 0.75 \(\mu\)s, respectively, which is superior to...
those of the Ge detector (with rise and decay times of 2.06 and 2.52 μs, as shown in Fig. S12f†).

Table 1 summarizes the device parameters of our device and some other photodetectors tested without bias. As evident, both the response range and response speed are superior to those of
Table 1  Detection performance of some current self-powered photodetectors

<table>
<thead>
<tr>
<th>Device structure</th>
<th>Wavelength (nm)</th>
<th>R (A W⁻¹)</th>
<th>D* (Jones)</th>
<th>Response time (µs)</th>
<th>Response range (nm)</th>
<th>Years</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₂Te₃/WSe₂</td>
<td>633</td>
<td>20.5</td>
<td>NA/NA</td>
<td>180/210</td>
<td>~1550</td>
<td>2019</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>1550</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb₂Te₃/Si</td>
<td>1550</td>
<td>0.15</td>
<td>5.76 × 10¹²</td>
<td>98/133</td>
<td>~1550</td>
<td>2022</td>
<td>48</td>
</tr>
<tr>
<td>MoS₂/CdTe</td>
<td>780</td>
<td>0.037</td>
<td>6.10 × 10¹⁰</td>
<td>43.7/82.1</td>
<td>~1700</td>
<td>2018</td>
<td>49</td>
</tr>
<tr>
<td>Sb₂Se₃/ZnO</td>
<td>625</td>
<td>0.173</td>
<td>2.25 × 10¹¹</td>
<td>37/104</td>
<td>~980</td>
<td>2022</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>930</td>
<td>0.074</td>
<td>9.10 × 10¹⁰</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb₂S₃/TiO₂</td>
<td>530</td>
<td>3.38</td>
<td>2.84 × 10¹¹</td>
<td>20/15</td>
<td>~700</td>
<td>2022</td>
<td>51</td>
</tr>
<tr>
<td>CsBi₃I₁₀/SnO₂</td>
<td>650</td>
<td>0.20</td>
<td>1.70 × 10¹¹</td>
<td>7.8/8.8</td>
<td>~740</td>
<td>2021</td>
<td>52</td>
</tr>
<tr>
<td>AgSbS₂/TiO₂</td>
<td>620</td>
<td>0.09</td>
<td>3.70 × 10¹⁰</td>
<td>6/34</td>
<td>~900</td>
<td>2023</td>
<td>31</td>
</tr>
<tr>
<td>AgSb₄(Se)/CdS</td>
<td>660</td>
<td>0.4</td>
<td>5.32 × 10¹¹</td>
<td>1.12/0.75</td>
<td>~1920</td>
<td>2023</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>0.12</td>
<td>1.62 × 10¹¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1550</td>
<td>0.012</td>
<td>1.71 × 10¹⁰</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

most of the listed self-powered photodetectors. This fast response speed can be directly attributed to the special gradient device structure, where the composition near the p–n junction interface in the depletion region has a relatively wide band gap, providing a high built-in potential conducive to the rapid separation of photo-generated charge carriers. Moreover, the materials outside the p–n junction interface are highly seleniumized, offering broad absorption for infrared light as well as facilitating ease of charge transport. The results suggest that this photodetector can monitor high-frequency near-infrared light signals, making it promising for applications in ultrafast-switching infrared signal detection, such as the laser communication field.

3 Conclusions

We have developed a novel method for preparing highly seleniumized AgSb(S,Se)₃ thin films with a significantly narrower energy band gap through spray pyrolysis, coupled with modification using indium nitrate. This innovative approach has led to a substantial extension of the response range from 760 to 1920 nm for the AgSbS₂ photodetector. The optimized photodetector demonstrated remarkable responsivity, reaching 5.57 mA W⁻¹, and an impressive detectivity of 7.43 × 10⁹ Jones at 1550 nm. Moreover, it showcased a high bandwidth of up to 0.3 MHz, along with rapid rise and decay times of 1.12 µs and 0.75 µs. These exceptional response range and speed characteristics surpass the performance of most reported self-powered photodetectors. Given its outstanding performance, our photodetector holds great promise for applications in high-speed photon computation and communication. With its capability to detect a wide range of infrared wavelengths and its fast response speed, the device creates exciting opportunities for ultrafast-switching infrared signal detection, especially in the field of laser communication. Additionally, we have developed a model that explains material crystallization from a solution containing a inconsistent crystallization component associated with spray pyrolysis deposition. This model is helpful in optimizing optical and electrical performance for various infrared absorbers, potentially providing new possibilities for developing high-performance broadband photodetectors through the reconstruction of existing compound semiconductors.

Data availability

The data used to support the findings of this study are available from the corresponding author upon request.

Author contributions

Zhen Zhang: formal analysis, investigation, methodology. Jiang Cheng: formal analysis, investigation, methodology, writing – original draft. Xin Yang: conceptualization, review & editing. Dongyu Bai: formal analysis, validation. Hua Tang: formal analysis, data curation. Xihao Chen: conceptualization, methodology. Shenghao Wang: conceptualization, writing, review & editing. Lu Li: resources, conceptualization, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Key R&D Program of China (Grant No. 2022YFB3603202), the National Natural Science Foundation of China (Grant No. 62171069), Cooperation projects between universities at Chongqing and institutes affiliated to the Chinese Academy of Sciences (HZ2021019), the Natural Science Foundation of Chongqing (CSTB2023NSCQ, LZX0058, and 20211201), and Scientific and Technological Research Program of the Chongqing Municipal Education Commission (KJQN202301315, KJZD-K201901302, and KJQN202101335).
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