Ultrafast and Broadband Photodetection Based on Selenized $AgSbS_2$ Thin Films Prepared by Spray Pyrolysis Deposition and Modified by Indium Nitrate

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1. Experimental

Preparation of $AgSbS_2$(Se) films: $AgSbS_2$ precursor film were firstly prepared on CdS films by ultrasonic spray pyrolysis (USP) method at a deposition rate of 20 nm min^{-1}. The spray solution was prepared as by dissolving 0.5 mmol silver nitrate, and 0.25 mmol indium nitrate (99.9%, Macklin), and 2 mmol thiourea into 7.5 mL 2-Methoxyethanol (99.9%, Macklin), 0.5 mmol antimony acetate(99.9%, Aladdin) into 2 mL acetic acid. Before that 0.3 ml acetic acid and 0.05 mL nitric acid was dropped into the solvent to prevent alcoholysis of antimony acetate. In order to optimize film structure and morphology, some indium nitrate was added to spray solution. During the USP deposition, the nozzle was mounted at a distance of 30 mm above the heating block. Compressed N_2 gas were used as the carrier gas with a rate of 20 L min^{-1}. The solution atomization rate was accurately tuned at 0.3 mL min^{-1}. Then, the prepared $AgSbS_2$ precursor films were transferred to a controlled dual-temperature zone rapid thermal processing furnace. The thermal selenidation process was fine

tuned to a condition where Se powder was heated at 350 °C and precursor films was heated at 400°C for 10 min.

Photodetecors Fabrication: A 100 nm thick CdS buffer layer was deposited on the ITO substrate by chemical bath deposition at 80 °C and then annealed at 400 °C in the air for 5 min. Then $AgSbS_2(Se)$ film was prepared on CdS as described above. Lastly, patterned Au back-contact electrodes with thickness of 80 nm were successively sputtered onto the top of $AgSbS_2(Se)$ in an ion sputtering coater.

Material Characterization:

Morphology and elemental distribution were measured by high resolution field emission scanning electron microscopy (SEM, Zeiss Merlin) coupled with an energy dispersive x-ray spectroscopy (EDXA, Oxford Instruments). The phase of the film was checked with X-ray diffraction (XRD, Bruker D8). The HAADF/STEM images and electron diffraction patterns were performed on a FEI Titan Themis Z microscope equipped with a probe-forming aberration corrector and operated at 300 kV. The absorptance were measured using a UV–Vis–IR spectrophotometer (Agilent Cary 5000). The electronic structure was conducted by an X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi). The thickness of the films was measured using a stylus profile meter (Alpha-Step D-100).

Device Characterization:

The J-V characteristic was recorded by using a Keithley 2450 source meter under different irradiation condition, Electrochemical impedance spectroscopy was conducted by using an electrochemical workstation (Shanghai Chenghua 760e) at zero-bias. Frequency response of photodetector was recorded by the oscilloscope under the irritation of 980 nm laser. Photocurrent response to on/off light irradiation was recorded by using Keithley 2450 source meter, the on/off and interval of which was controlled by a relay-operated controller.

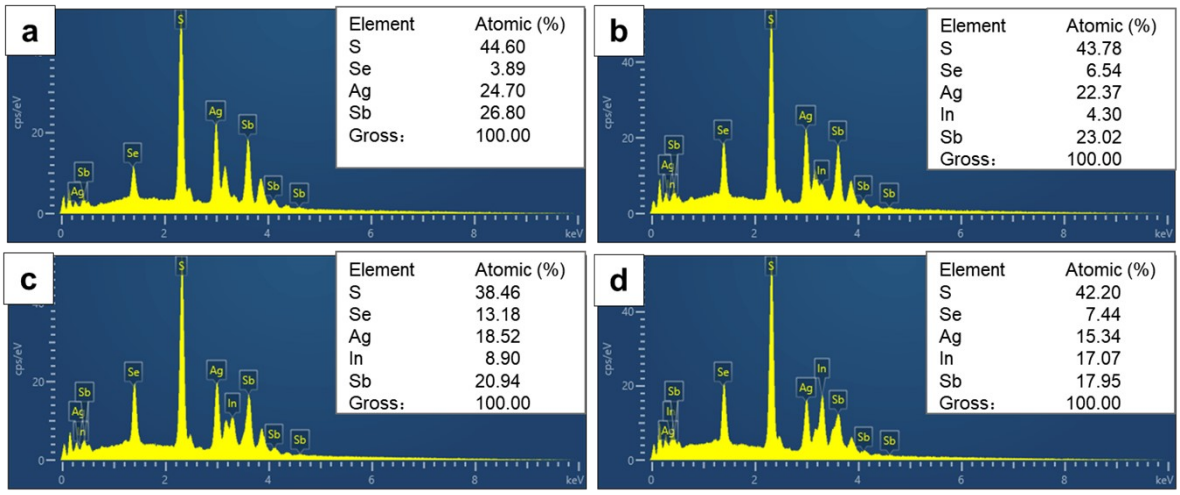

Figure S1. The EDS analysis for $AgSbS_2(Se)$ films that selenized for 4 min with different indium concentration. (a) In/Sb=0, (b) In/Sb=0.2 (c) In/Sb=0.5 and (d) In/Sb=1

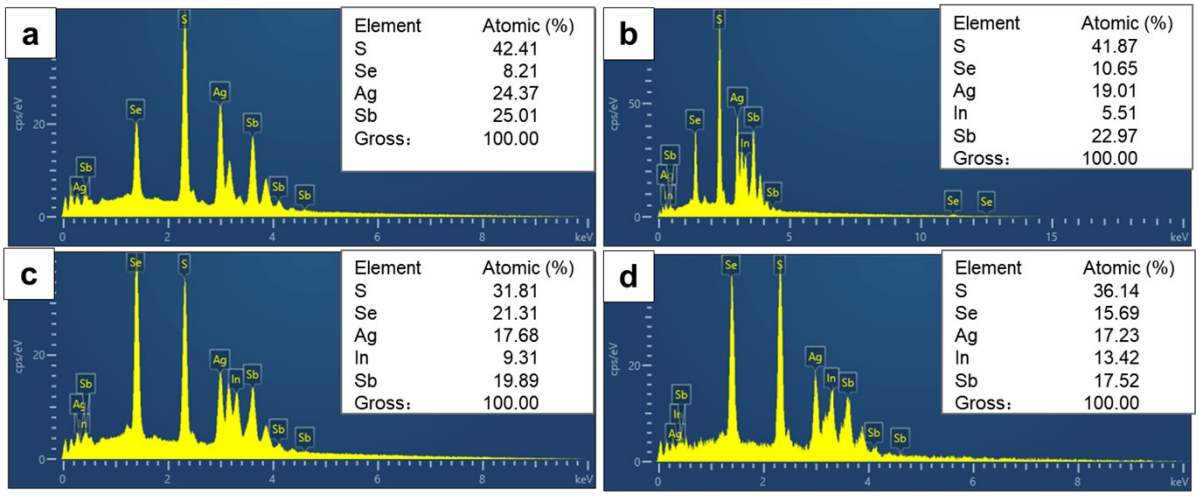

Figure S2. The EDS analysis for $AgSbS_2(Se)$ films that selenized for 7 min with different indium concentration. (a) In/Sb=0, (b) In/Sb=0.2 (c) In/Sb=0.5 and (d) In/Sb=1

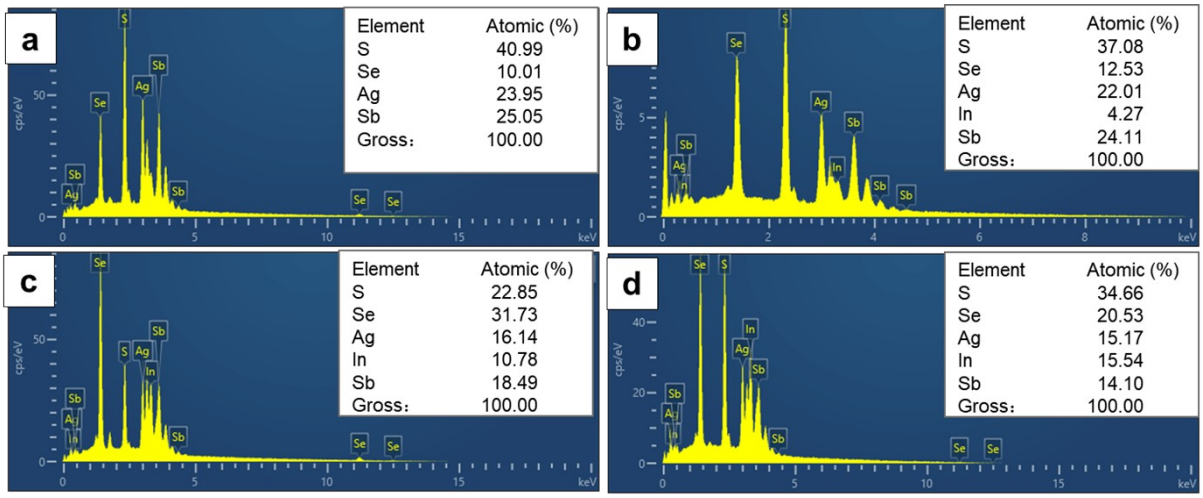

Figure S3. The EDS analysis for $AgSbS_2(Se)$ films that selenized for 8 min with different indium concentration. (a) In/Sb=0, (b) In/Sb=0.2 (c) In/Sb=0.5 and (d) In/Sb=1

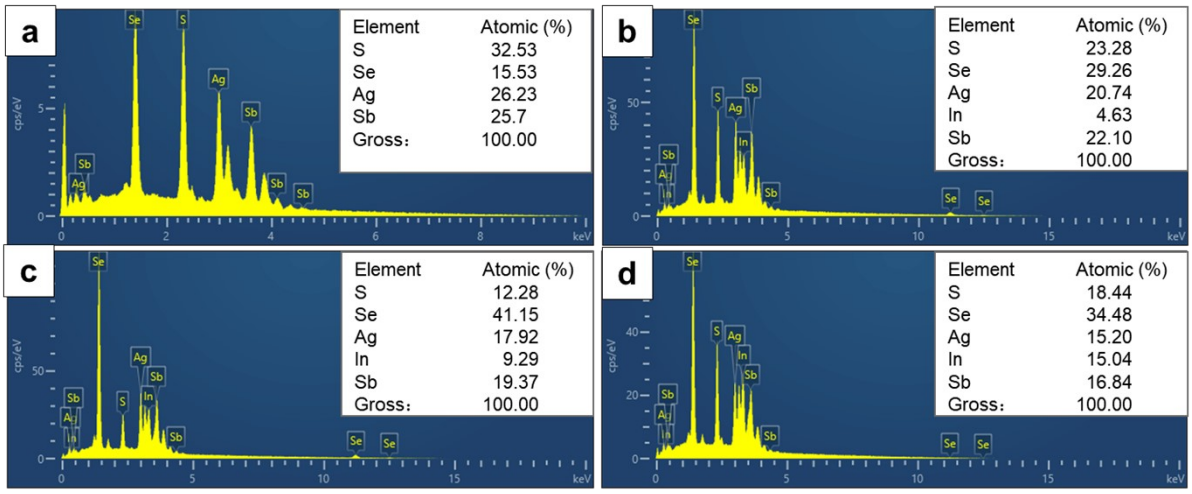

Figure S4. The EDS analysis for $AgSbS_2(Se)$ films that selenized for 10 min with different indium concentration. (a) In/Sb=0, (b) In/Sb=0.2 (c) In/Sb=0.5 and (d) In/Sb=1

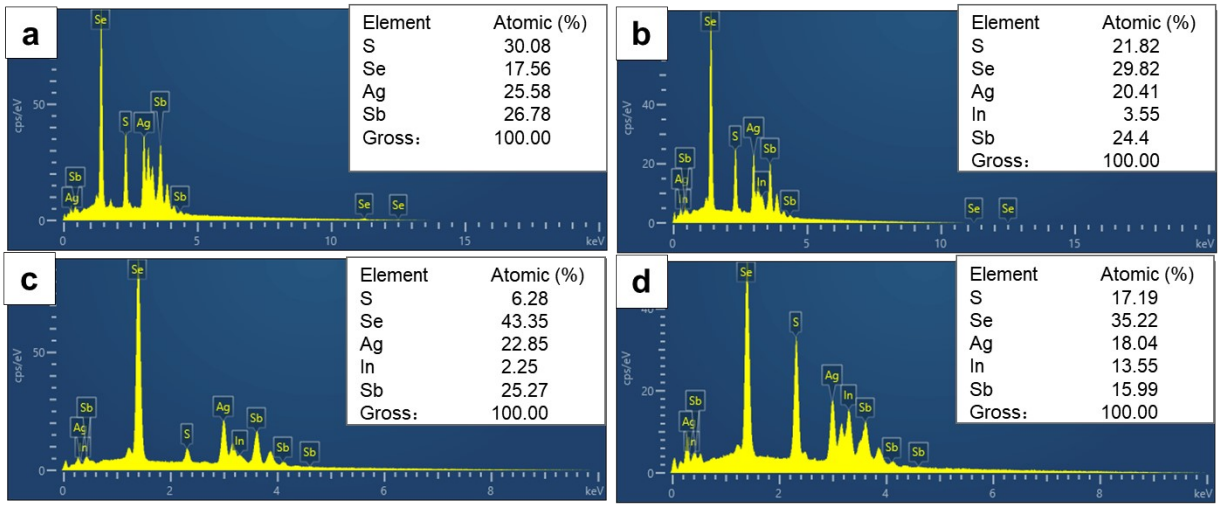

Figure S5. The EDS analysis for $AgSbS_2(Se)$ films that selenized for 12 min with different indium concentration. (a) In/Sb=0, (b) In/Sb=0.2 (c) In/Sb=0.5 and (d) In/Sb=1

Table S1. EDS quantitative analysis for $AgSbS_2(Se)$ films with and without indium

In/Sb in spray solution	Se/(S+Se) (%)				
	4min	7min	8min	10min	12min
0	8.02	16.22	19.63	32.32	33.77
0.2	12.99	20.28	25.26	55.69	57.75
0.5	14.36	40.11	58.13	77.01	84.37
1	14.13	30.27	37.19	65.15	67.20

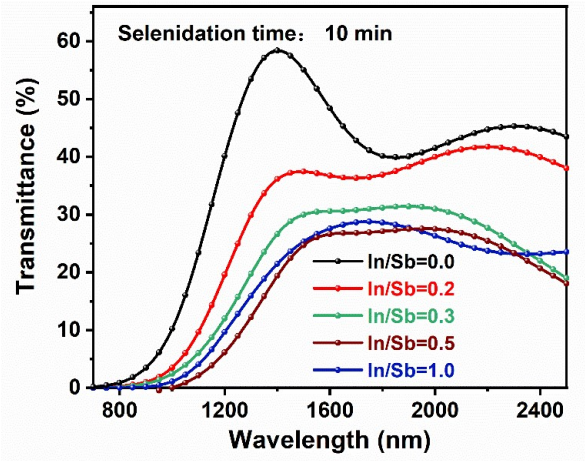

Figure S6. the Ultraviolet-Visible-near infrared (UV-Vis-NIR) spectrum of films with different In/Sb ration selenized for 10 min.

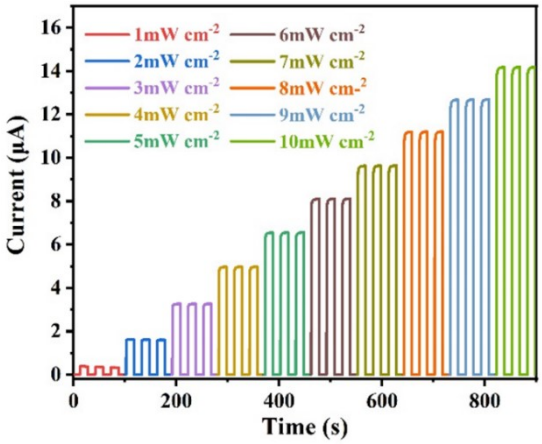

Figure S7. Photocurrent response of indium-free photodetector to on/off light at different power densities of 660 nm.

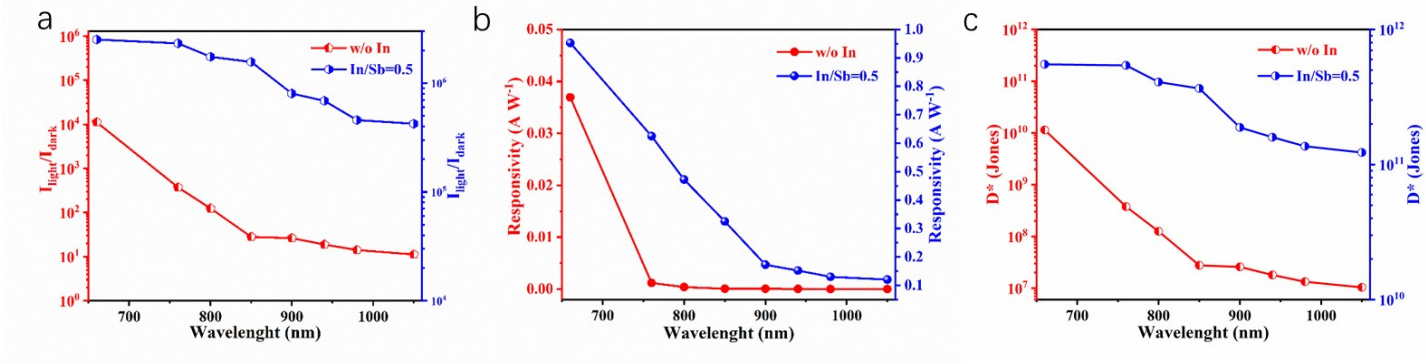

Figure S8. Supplementary comparison of response for $AgSbS_2$/CdS heterojunction device without and with indium. The comparison of (a) switching ratio, (b) responsivity, (c) detectivity for the two photodetectors.

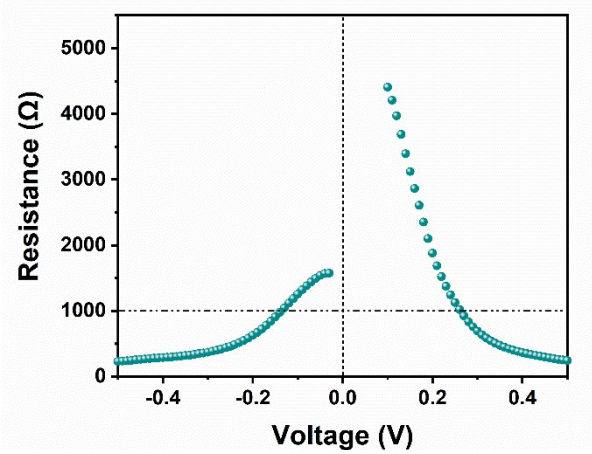

Figure S9. Resistance of the devices derived from J-V curve test in dark.

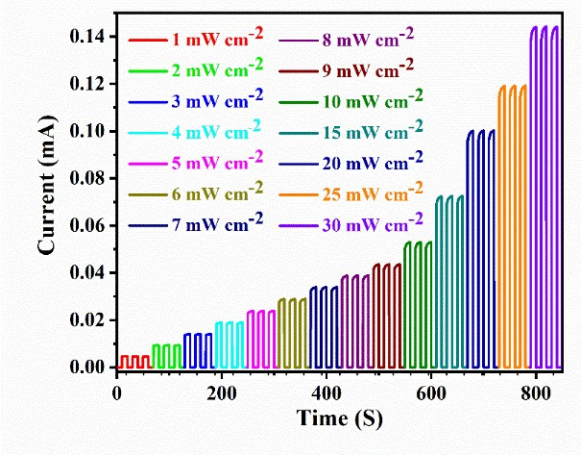

Figure S10. Photocurrent response to on/off light of photodetector irradiated in 1050 nm light with different power density from 1 to 30 mW cm^{-2}

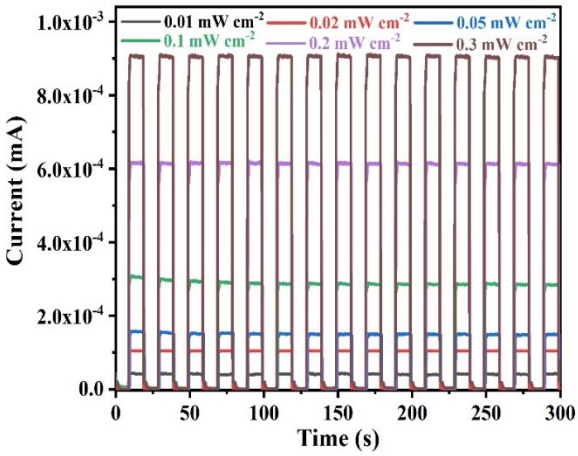

Figure S11. Photocurrent response to on/off light of photodetector irradiated in weak irradiation with the power density lower than 0.3 mW cm^{-2}

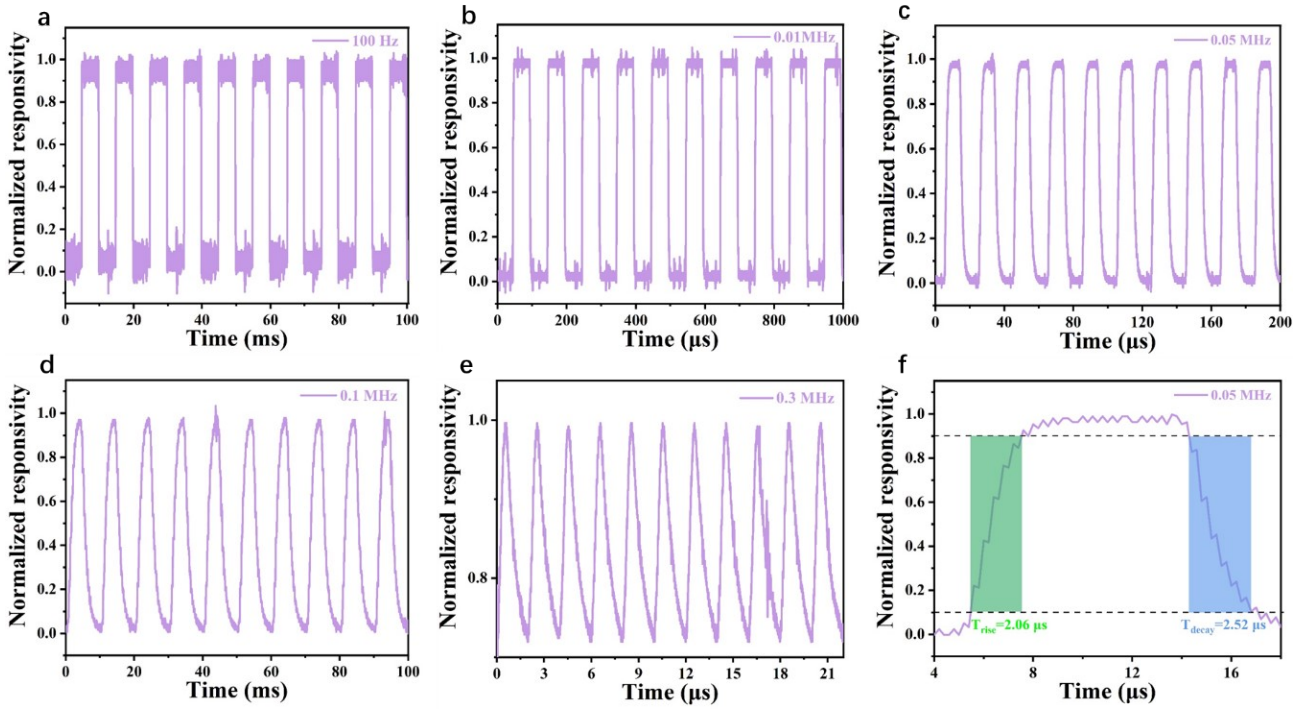

Figure S12. Frequency response of photodetector on 980 nm laser. The response of the Ge detector to square wave incident light source with the frequencies of (a) 100Hz, (b) 0.01MHz, (c)0.05MHz, (d) 0.1 MHz. (e) 0.3MHz, and (f) response time of the photo detector.