[1]Detrapping of the Carriers from Shallow States in Highly Responsive, Fast, Broadband (UV-Vis-NIR), Self-Powered SnSe/Si Photodetector with Asymmetric Metal Electrodes

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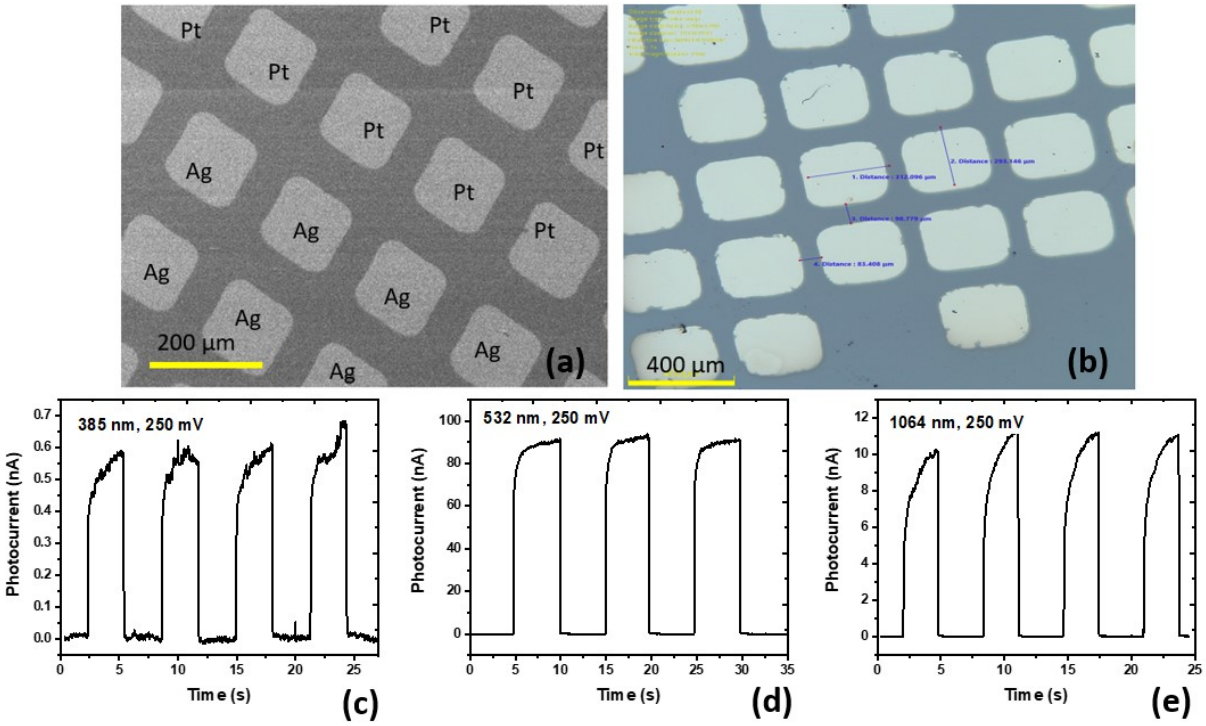

Figure S1. (a) Optical image of the device Si/SnSe, (b) Si, (c) photodetection of the bare n-Si device under 385, (d) 532, and (e) 1064 nm at 250 mV bias.

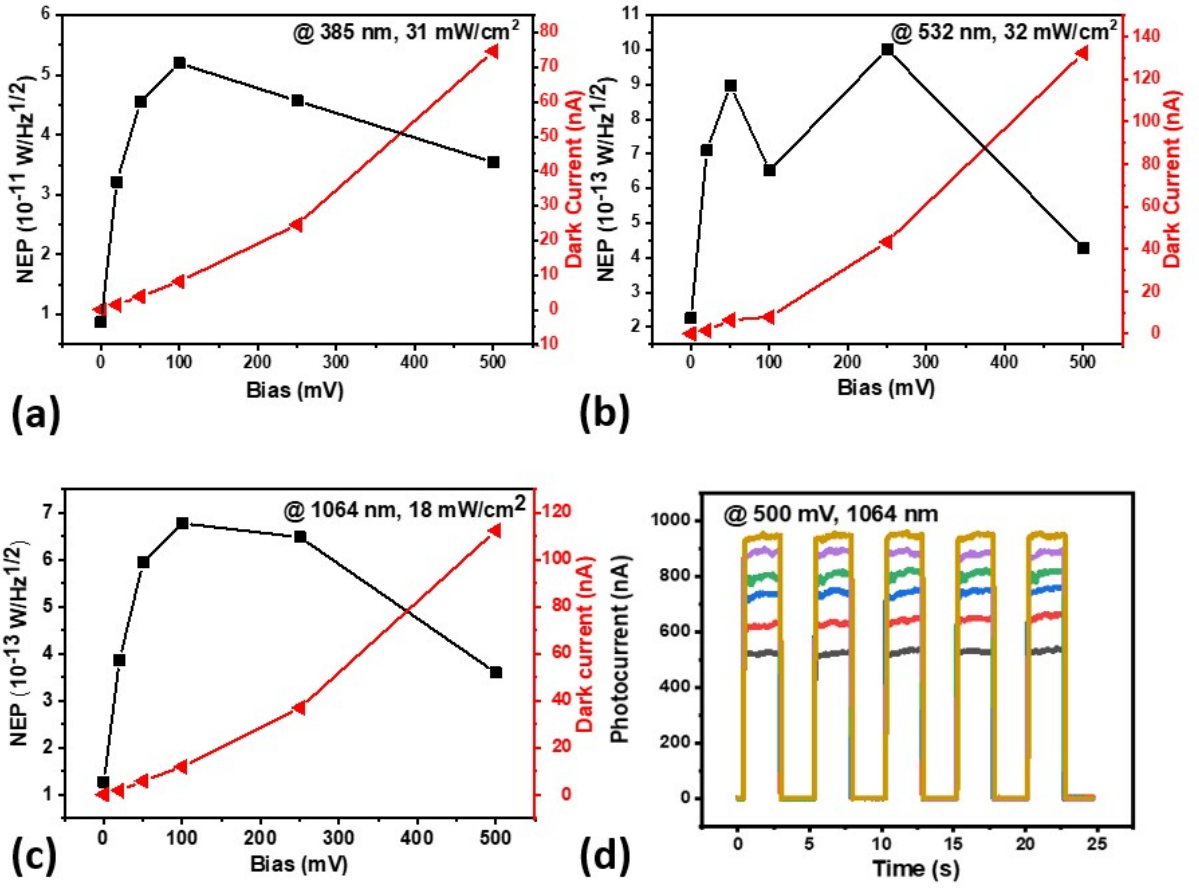

Figure S2. NEP and dark current at (a) 385 nm, (b) 532 nm, (c) 1064 nm, and (d) photocurrent at different power densities at 1064 nm laser at 500 mV bias.

Ultrafast transient spectroscopy:

We conducted a study utilizing power-dependent transient reflectance spectroscopy to investigate the presence of defects and their impact on carrier transport across the junction. Sample geometry was such that reflectance can be treated the same as absorption. The sample was excited well above the material's band gap at 650 nm (1.9 eV) and detected within a broad near-infrared (NIR) range spanning from 850 nm to 1500 nm. The behavior of carriers was monitored over a wide time-delay window, reaching up to 6 ns. **Figure S3**(a-f) below illustrates the transient reflectance spectra at different pump laser power, specifically 0.25 mW, 0.50 mW, and 1 mW, and their kinetics at different wavelengths. Differential reflectance spectra are taken similar to differential absorption due to the geometry of the sample[1] [2].

First, take the case of the 0.25 mW fluence spectra (figure S3 (a)); the spectra exhibit three distinct features: a positive signal centered around the 900 nm range, followed by a negative signal centered at 1040 nm and, beyond 1200 nm, another positive sign. Positive peaks around 900 nm and beyond 1200 nm show induced absorption signature. This absorption shows the transition from the conduction band or the shallow traps below the conduction band minima to higher excited states. Power-dependent fluence transient spectra were taken at 0.5 and 1 mW to assign the exact nature to the positive peak. In all cases, the spectra exhibit similar characteristics, with the distinction lying in the increasing difference transient reflectance (TR) with increasing power. If they exist, the shallow traps should be limited and show saturation behavior with fluence [3][4]. From **Figure S3** (c and e), both the positive peaks around 900 nm, and beyond 1200 nm shows saturation behaviour. Peak beyond 1200 nm may be due to absorption from the trap states to the conduction or higher excited states.The peak around 900 nm may be due to the absorption from eighter conduction or traps to the higher conduction states, because of the higher energy in nature. The negative signal attributed to GSB

corresponds to the material's band-to-band transition, reflecting the band gap and decay of shallow trap carriers to the valence band.

Notably, it is observed that as the power increases, each of these characteristic signals undergoes a blue shift, which has significant value shifts from 1040 to 1016 nm. The observed blue shift, which intensifies with increasing power, is ascribed to a higher carrier concentration, resulting in a band-filling effect that causes a change in the band gap (figure S4). Notably, the Ground-State Bleaching (GSB) signal at 1040 nm undergoes a rapid decay within a few picoseconds, followed by a notable shift to 920 nm within the subsequent picosecond at all powers. The shift may be understood like this: when there is a higher concentration in the conduction band, there is no transition of the shallow trapped carriers to the conduction band. But after some time here (3ps), most carriers decay via bimolecular recombination. There is a very low concentration of the excited carriers, and shallow trapped carriers, which are in the thermal equilibrium to the conduction band states, can transition to the conduction band. Hence, these shallow trapped carriers decay via the transition to the conduction band.

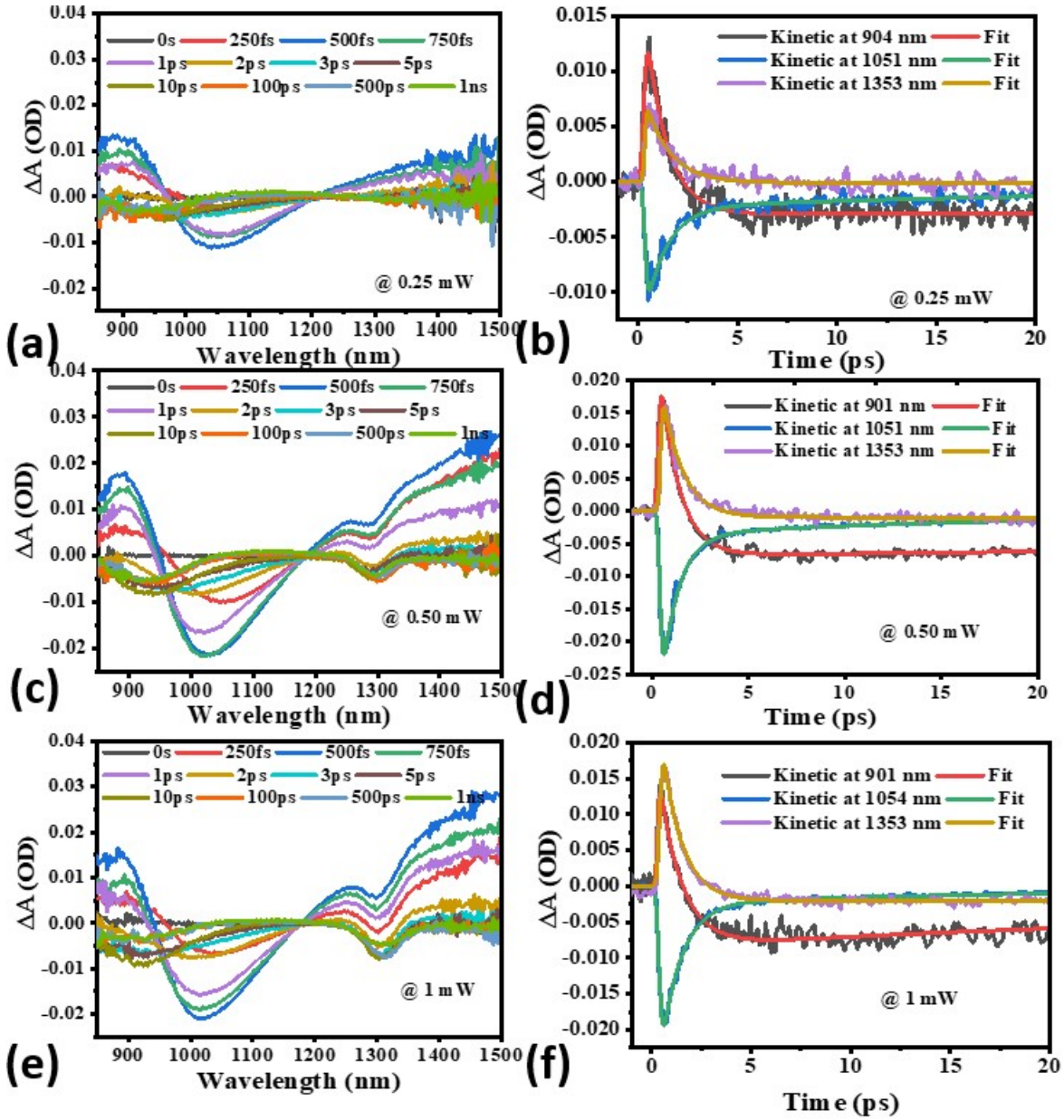

Figure S3. Transient spectra (differential absorption) and their kinetics at different fluences (a), (b) for 0.25 mW, (b), (c) 0.50 mW, and (d) and (e) 1 mW.

We conducted kinetic profile fitting at various probe wavelengths using a multi-exponential fitting model with the Surface Xplorer software. The time constants derived from this fitting provide insights into the power-dependent relaxation of carriers [5] (see **Table S1**). When examining the kinetic profile at 900 nm probe wavelength, we observed distinct behaviours depending on the excitation power. At lower power levels (0.25 mW), the profile was best described by a single time constant, primarily associated with intra-band relaxation

within the material's band. The second component with a timescale exceeding 6 ns was evident, indicative of carrier trapping and subsequent recombination.

In contrast, at higher excitation power levels at the same probe wavelength, the kinetic profile was fitted with a three-exponential model. It enabled the differentiation between recombination and trapping processes, represented by three distinct time constants. The time (t1), which is intra-band relaxation, becomes faster for the higher fluences attributed to more significant carrier interaction with increased carrier concentration. The other two, shorter timescale (t2), in the order of tens of picoseconds, corresponded to carrier recombination, and the component with a timescale (t3) greater than 6 ns was attributed to trapping. The prolonged carrier lifetime observed in the Photo-Induced Absorption (PIA) signal at 900 nm with increasing power can be ascribed to larger carrier tapping and slow recombination.

Additionally, for the PIA signal beyond 1200 nm, we observed a significantly faster decay with increasing power, depicted in **Table S1** below. This phenomenon is linked to the increased carrier density, which causes faster carrier interactions and, consequently, faster relaxation and recombination. We have excited the carriers at 1064 nm for the device, so an insight into the 1050 nm wavelength should be considered.

We observed a faster decay with increasing power when fitting the kinetic profile for the Ground-State Bleaching (GSB) signal. This behavior can be attributed to reduced carrier trapping. The reduced trapping depicts the lesser concentration of trap states corresponding to these energy states (at higher fluence, part of the concentration of trapped carriers becomes much less than the lower fluence. The kinetic profile is fitted by 3 exponentials for lower fluence and by two exponentials fit at higher fluences, which owes to the fact that lesser carriers got trapped at higher fluences and faster recombination. These excess carriers tend to recombine more readily, thus accelerating the decay of the GSB signal. The kinetic fit at the

1050 nm shows the three-exponential fitting, t1 (1.1 *p*s), for the carrier relaxation in the conduction band for the 0.25 mW fluence. At the same time, t2 (24.6 *p*s) and t3 (1.12 ns) show the recombination and trapping times for the carriers. At higher fluences, dynamics is well fitted by the 2 exponentials; hence, there are no third (trapping) components. When this trend is extrapolated for the lower fluence, it can be concluded that few carriers are trapped for a significant time. The shallow states that exist here play the role of trapping states.

Table S1 shows that carriers are trapped at lower fluences, and trapped carrier concentrations decrease with pump fluences due to limited states. Hence, the trapping states exist in the device but have significantly lower concentrations. In summary, the multi-exponential fitting of kinetic profiles at various probe wavelengths reveals distinct carrier relaxation behaviors influenced by excitation power. These behaviors are associated with intra-band relaxation, recombination processes, and carrier trapping, and they provide valuable insights into the material's response to varying excitation.

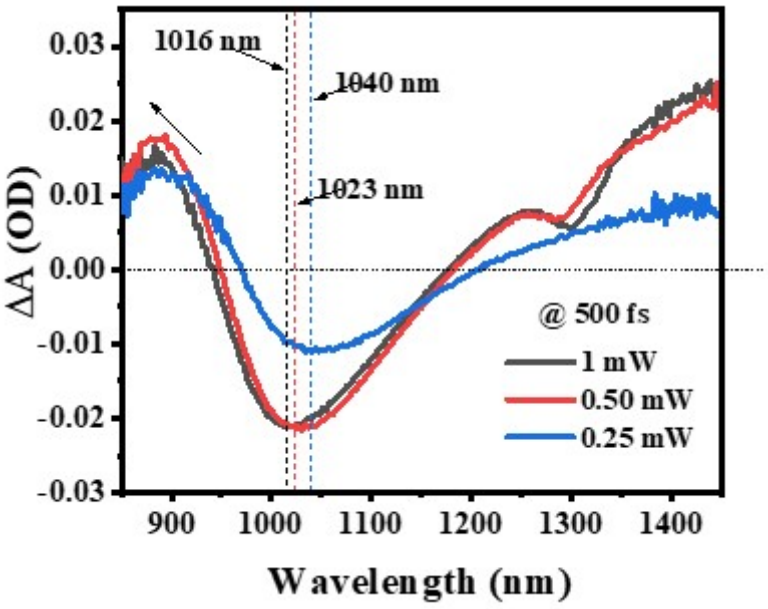

Figure S4. Comparative transient spectra at different fluences.

Sample / Substrate excitation @ 650nm	Wavelengths (In nm)	Lifetime τ_1(ps) Amplitude A_1(%)	τ_2(ps) Amplitude A_2(%)	τ_3(ps) Amplitude A_3(%)	Average Lifetime (ps)
0.25 mW	900	1.07 (87 %)	----------	> 5 ns (13 %)	0.927
	1050	1.1 (81 %)	24.6 (15 %)	1120 (4 %)	70.28
	1350	1.22 (90%)	56.5 (5%)	> 5 ns (5 %)	3.928
0.50 mW	900	1.00 (82 %)	60.4 (7 %)	> 5 ns (11 %)	5.046
	1050	0.85 (87 %)	21.2 (13 %)	----------	3.47
	1350	1.05 (96 %)	----------	> 5 ns (4 %)	1.008
1 mW	900	1.16 (75 %)	30.2 (17 %)	> 5 ns (8 %)	5.939
	1050	1.00 (89 %)	26.3 (11 %)	---------	3.665
	1350	0.99 (93 %)	2.96 (3.9%)	> 5 ns (3.1 %)	1.18

Table S1. Kinetics of the different mechanisms at different fluences for *n*-Si/SnSe.

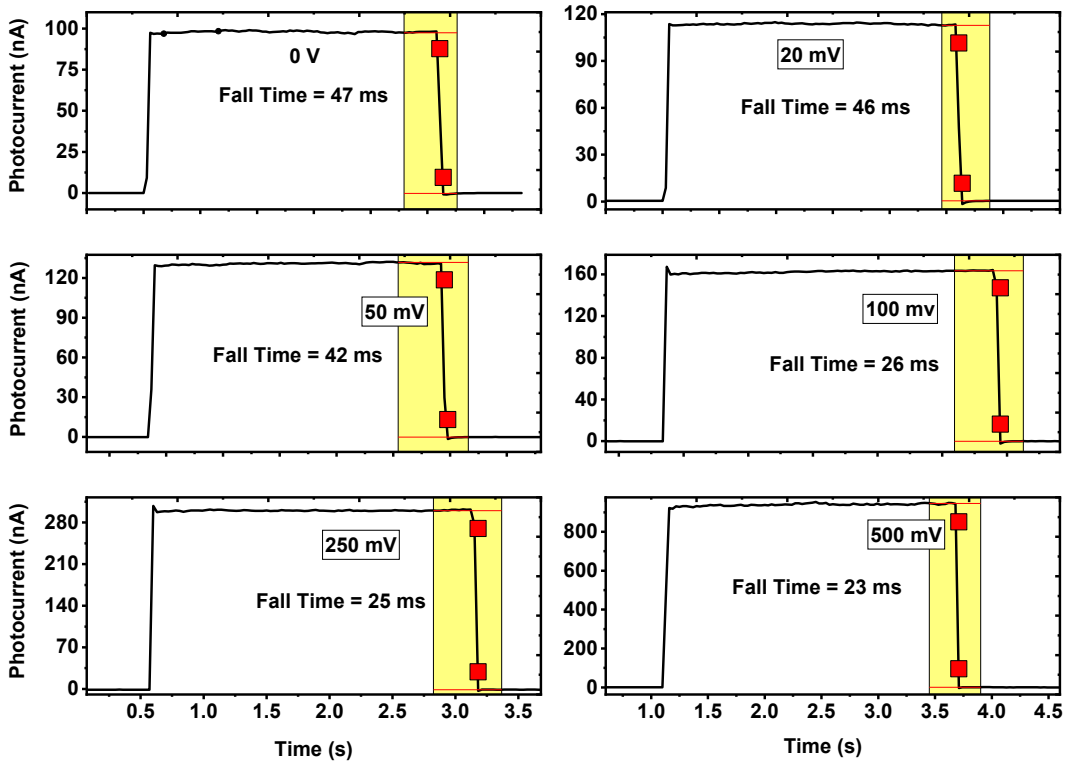

Figure S5. Recovery time of the device under different voltages at 18 mW/cm^2 power density.

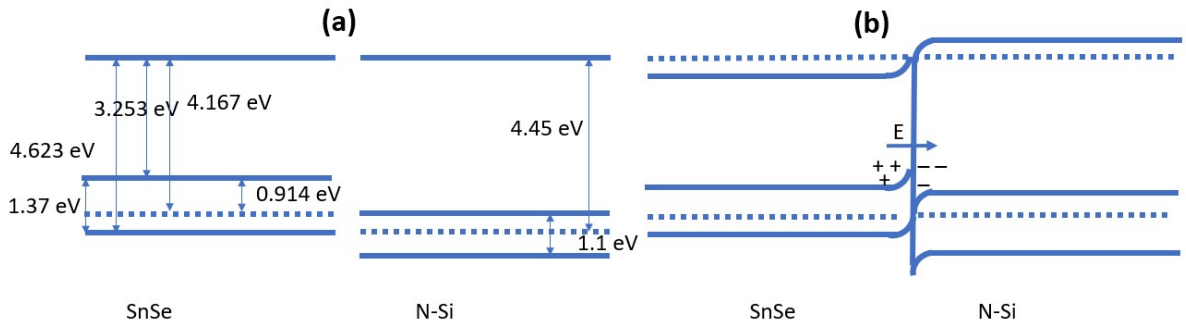

Figure S6. Energy band alignment of the n-Si and SnSe (a) before and (b) after deposition.

References

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