Supporting Information

Spectromicroscopy and Imaging of Photoexcited Electron Dynamics at in-plane Silicon *pn* Junction

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Supplementary figures

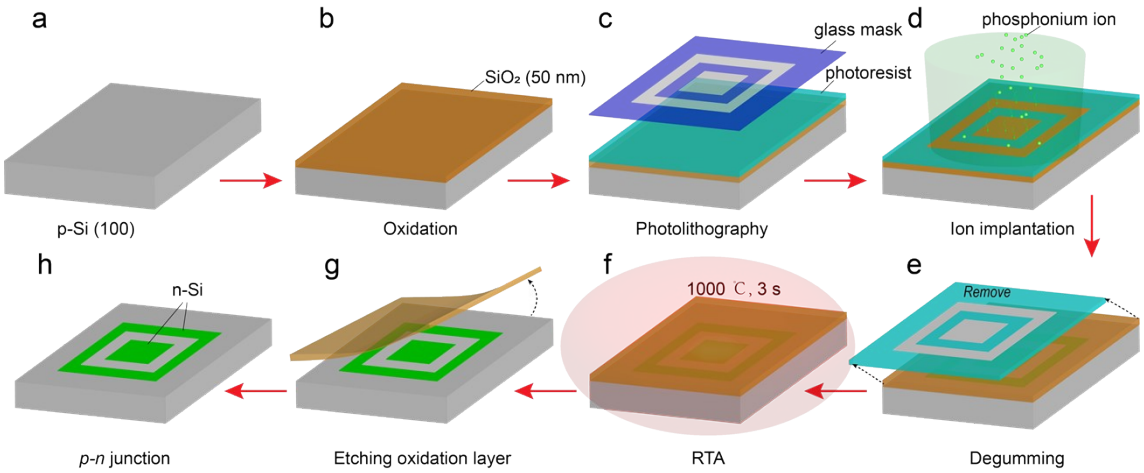

Figure S1. Schematic of processes of the sample fabrication. (a) The substrate is *p*-type silicon (100) with a resistance of ~0.05-0.20 Ω·cm. And the doping level of the *p*-type substrate is about ~10^{17} atom/cm^3. (b) Oxidation process. The thickness of SiO_2 (orange layer) is ~50 nm. (c) Photolithography. Transfer the photomask (top, the blue region indicating light shading area, and the white region indicating transparency light area) to the photoresist (cyan layer). (d) Phosphonium ion implantation. The energy of the phosphonium ion is ~80 keV during the implantation process. And the *n*-type patterns have a doping level of about ~10^{19} atom/cm^3. (e) Wet and dry removal of photoresist. (f) Rapidly thermal annealing (RTA) under 1000 ℃ for 3 seconds. (g) Etching the SiO_2 oxidation by the HF. (h) Formation of the in-plane *p*-*n* junction.

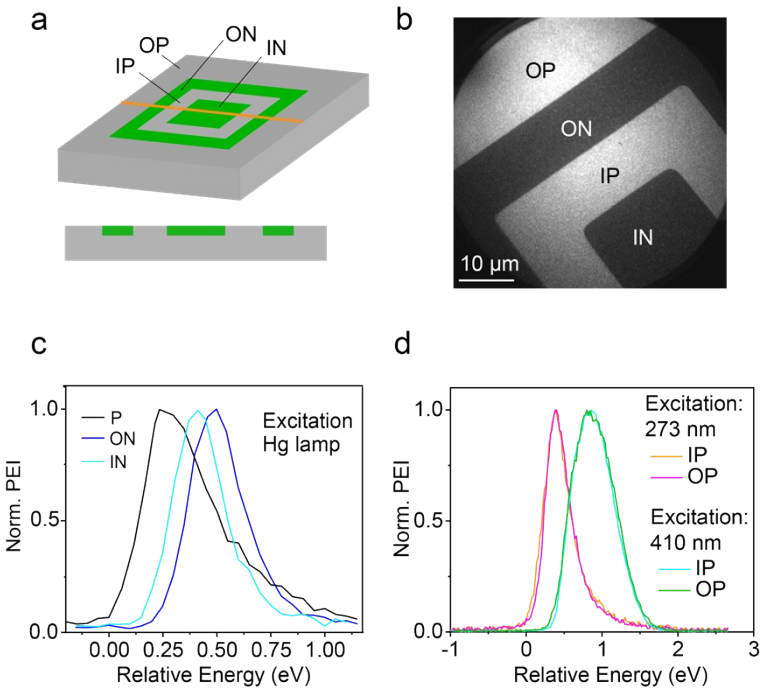

Figure S2. Photoelectron spectroscopy of the OP region and IP region. (a) Schematic of the *pn* junction. Bottom: Profile of the sample along the orange line. (b) PEEM image photoexcited by the 410 nm laser. (c) The photoemission spectroscopy is excited by the Hg lamp with a photon energy of ~4.9 eV in the ultraviolet (UV) range. Photoemission electron kinetic energy of the P regions (black line) is lower ~0.25 eV than that of the ON regions (blue line). The energy difference of IN (cyan line) and ON (blue line) regions is about ~0.10 eV. Note: the x-axis indicates the relative energy of the photoemission electrons rather than the real kinetic energy. (d) Photoelectron spectroscopy excited by the 273 nm laser (orange for IP, and magenta for OP region) and 410 nm laser (cyan for IP, and green for OP region).

Table S1. The linewidth of the photoelectron spectroscopy. The '273 nm' and '410 nm' refer to the 273 nm pulsed laser and 410 nm pulsed laser.

Regions \ Excitation laser	273 nm	410 nm
P in junction 1	382 meV	701 meV
N in junction 1	302 meV	541 meV
P in junction 2	400 meV	663 meV
ON in junction 2	296 meV	550 meV
IN in junction 2	297 meV	540 meV

The photoelectrons spectroscopy excited by the 410 nm laser has a broader linewidth (about 700 meV and 550 meV for the P and N regions, respectively) compared with that excited by the 273 nm laser (about 400 meV and 300 meV for P and N regions, respectively) (shown the Table S1).

Here, we calculated the ratio of linewidth according to $R_{average} = \frac{\Sigma\left(\frac{L_{410}}{L_{273}}\right)}{n}$, where n is the number of the spectra used for calculations, L_{410} and L_{273} are the linewidths of the photoelectron spectroscopy excited by the 410 nm laser and 273 nm laser. Thus, the two-photon process's energy dispersion width is ~1.8 times as broader as that of the one-photon process.

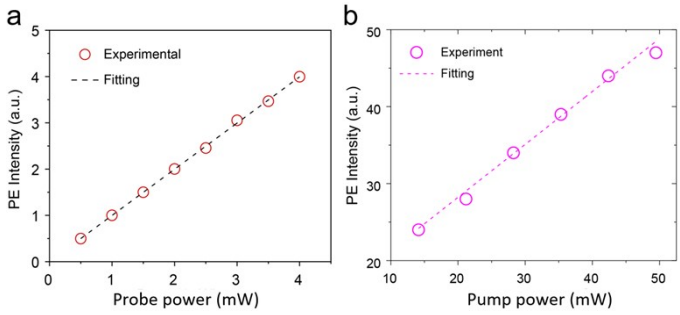

Figure S3. (a)The photoemission intensity as a function of probe power (red circles) at a fixed pump power of ~60 mW and a fixed delay time of ~0 ps. The photoemission signal is linear in probe power with a slope of 0.998. (b) The photoemission intensity as a function of pump power (magenta circles) at a fixed probe power of ~2 mW and a fixed delay time of ~0 ps.

For the static-PEEM condition, the power dependence results show that the 410 nm excitation is a two-photon photoionization process (multiphoton absorption), as shown in Fig. 1f in the main text. For the time-resolved PEEM condition, at the fixed delay time of ~0 ps, the photoemission intensity as a function of pump fluence (magenta circle) at a fixed probe power of ~2 mW shows a linear dependence, as shown in Fig. S3b. So the 410 nm excitation is in a linear range absorption in the time-resolved PEEM.

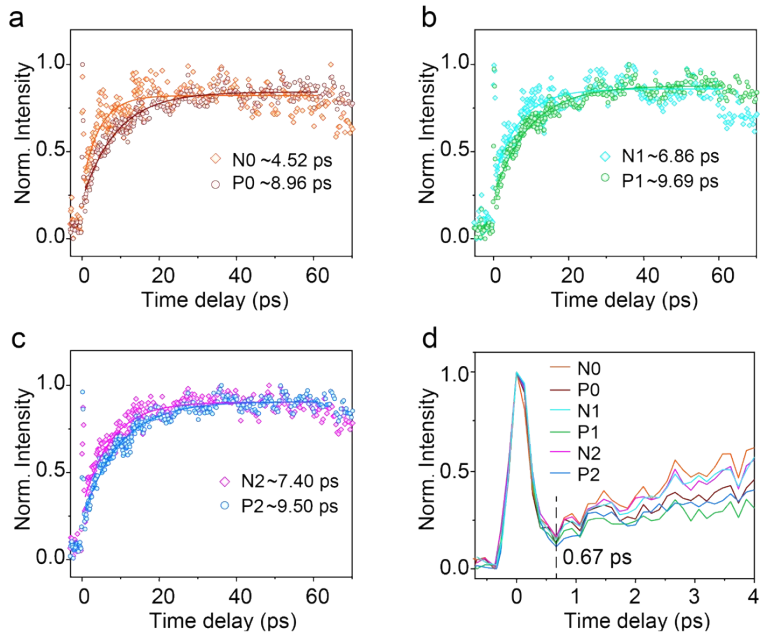

Figure S4. The comparison of the time traces of the normalized PE intensity of the P0/N0 junction (a), P1/N1 junction (b), and P2/N2 junction (c). (d) Enlarging the curves within ~4 ps.

Here we used the 80 MHz laser for the photoemission measurements, which has a pulse-pulse time separation of ~12.5 nanoseconds (ns). Since we measured the photoemission decay process within a ~100 ps time window, the measurement time scale is shorter than the typical carrier lifetimes for Si. The photoexcited electrons have no enough time to return to the ground states before the probe beam excitation. There would has a carrier accumulation in the conduction band minimum and then the carriers would return or scattering to the probe beam's detection window (purple regions in Fig. 4b), i.e., resulting in photoemission increasing. We note that such a phenomenon requires further investigation, perhaps by time-resolved angle-resolved photoemission electron spectroscopy.

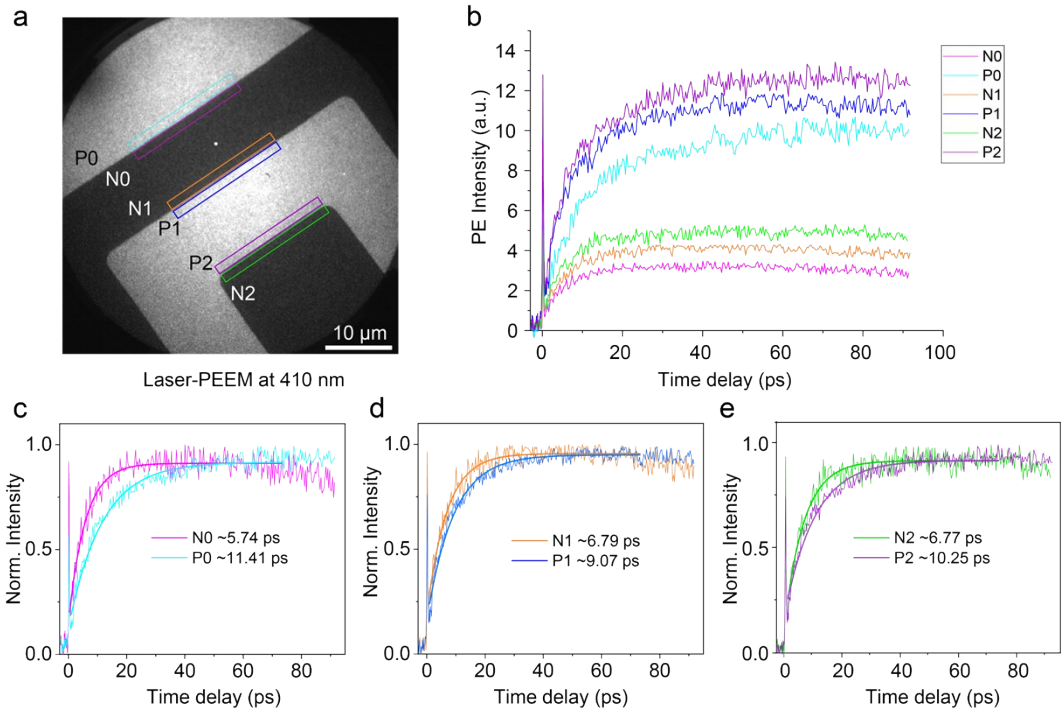

Figure S5. The time traces of the PE intensity measured by the 4 MHz pulsed laser. (a) The PEEM image of the *pn* junction excited by 410 nm laser. Rectangles highlight the areas over which the PE intensities are averaged. (b) The time traces of the PE intensity. And the comparison of the time traces of the normalized PE intensity of the P0/N0 junction (c), P1/N1 junction (d), and P2/N2 junction (e).

We should note that the spot diameter of the pump (410 nm) beam and the probe beam (273 nm) on the sample was about ~100 μm and ~60 μm, respectively. The pump and probe beams are coaxial, and the field of view (FOV) we select is 50 μm. So we state this is "Wide-field irradiation, wide-field detection." i.e., we obtained a series of images with FOV of ~50 μm under different time delays. Then we can analyze the images, and we selectively integrate the Photoemission (PE) intensity of the specific regions, such as the N0 (magenta), P0 (cyan) regions.

Here, we have also used the 4 MHz repetition frequency to measure the time-resolved PEEM images, as shown in Fig. S5. The signal to noise ratio (SNR) is much better. The 4 MHz laser has a pulse-pulse time separation of ~250 ns. And the time-resolved photoemission intensity excited by the 4 MHz pulsed laser show similar time traces to that by the 80 MHz lasers. But

the time traces shown in Fig. S5 need more time to reach the maximum point compared that by the 80 MHz lasers shown in Fig. 4c (main text) because of the larger pulse-pulse time separation.

Table S2. The characteristics of the PE time trace for Figure S4.

	Fast rise time (ps)	Fast decay time (ps)	Fast decay ratio	Rise time (ps)
N0	0.15	0.67	87 %	4.52
P0	0.16	0.67	84 %	8.96
N1	0.15	0.67	87 %	6.86
P1	0.16	0.67	84 %	9.69
N2	0.16	0.67	88 %	7.40
P2	0.16	0.67	85 %	9.50

Table S3. The number of photons under different laser illumination. The '410 nm + 273 nm' refers to the 410 nm, and 273 nm pulsed laser is used as the pump and probe light, respectively.

Excitation laser	273 nm	410 nm	410 nm + 273 nm
n	1.30 ± 0.01	2.28 ± 0.01	0.99 ± 0.01

Note 1: Discussion about the photoemission process

To illustrate the photoexcited carriers those can be accessed by 4.54 eV probe light in the band diagram, we drew a curve in the band diagram according to $\hbar k_{\parallel} = \sqrt{2m(nhv - E_b - \phi)}$, where nhv is the energy of the incoming photon (the parameter *n* refer to the Table S3 and Fig. S3), E_b is the binding energy, ϕ is the electron work function (equals to 4.7 eV [1]), *m* is the mass of the electron (equals to 0.51099895 MeV/c^2), $\hbar$ is the Plank constant (equals to 6.5821×10^{-16} eV·s), and $k_{\parallel}$ is the parallel momentum component of outgoing photo-electrons along the sample surface. The $k_{\parallel}$ is conserved after photoemission. The purple (blue) shaded area in Figure 3a (Figure 3b) shows the region of the band structure that can be accessed by the one-photon (two-photon) photoionization.

Note 2: Photoemission electrons relaxation dynamics

The rate equation for the relaxation of photoexcited electrons can be presented as the following:

$$\frac{dN}{dt} = -k_1 N + k_2 M - \frac{N}{\tau} \quad (1)$$

$$\frac{dM}{dt} = +k_1 N - k_2 M - \frac{M}{\tau} \quad (2)$$

Where *N* is the excited electrons density of the higher energy level in the conduction band (within the probe window of 4.54 eV photoionization), *M* is the electrons density near the conduction band minimum (out of the probe window of 4.54 eV photoionization), k_1 is related with the fast relaxation rate, k_2 is related with the rate that the electrons scattering from the conduction band minimum to the probe window, τ is the lifetime of the electrons and hole recombination. Considering the radiative recombination usually occurs on a much longer time scale (nanoseconds scale), the last item $-\frac{N}{\tau}$ ($-\frac{M}{\tau}$) can be ignored at a few picosecond scales.

$$\frac{dN}{dt} = -k_1 N + k_2 M \quad (3)$$

$$\frac{dM}{dt} = + k_1 N - k_2 M \tag{4}$$

It should be noted that the time trace of PE intensity we measured is related to the electron density of N(t). In other words, the electron density of M(t) cannot be measured, which is out of the probe window. The pump fluence of 410 nm pulse laser is about 19 μJ/cm^2. So the total photon density can be calculated as follows.

$$N_{total} = \frac{f}{h\upsilon} = \frac{19\mu J/cm^2}{6.63 \times 10^{-34} \times 7.5 \times 10^{14} J} = 3.8 \times 10^{13}\ cm^{-2} \tag{5}$$

The electrons density N(0) equals the total photon density times absorbance. The silicon's absorption is set as 3.7% (the absorption coefficient of silicon at 410 nm is 9.1354×10^4 cm^{-1}). Assuming each absorbed photon generates one pair of an electron and a hole, the resulting initial electron density N(0) is 1.4 × 10^{12} cm^{-2}. Near the X point, since the energy of 3.02 eV is insufficient to excite the electrons from the valence band to the conduction band, the M(0) is 0.

At the instant of excitation (N(0) $\gg$ M(0)), the fast decay process (k_1) dominates the dynamic, resulting in the PE intensity decreased. After tens of picoseconds, the scattering process (k_2) dominates the dynamic, resulting in increased PE intensity. The latter serves as a plausible mechanism for transferring electrons from the conduction band minimum to the probe window. Although we note that such a phenomenon requires further investigation, perhaps by time-resolved angle-resolved photoemission electron spectroscopy. And at the longer time scale (longer than 50 ps), the PE intensity starts to decrease due to the electron-hole recombinations ($-\frac{N}{\tau}$ starts to dominate the decay process). The phenomenon is consistent with the previous report by Zewail's group [2]. The fast decay time (τ_1=1/k_1) and the rise time (τ_2=1/k_2) can be estimated from the experimental data, shown in Table S2.

Supplementary Movie | Video of the evolution of photoexcited electrons in in-plane silicon *p-n* junction

The movie shows pump-probe PEEM signals at a series of time delays with the pump pulse 410 nm (60 mW) and the probe pulse 273 nm (4 mW) at normal incidence.

Reference

1 F. G. Allen and G. W. Gobeli, *Phys. Rev.,* 1962, **127**, 150-158.

2 T. D. S. Ebrahim Najafi, Jau Tang, Ahmed Zewail, *Science,* 2015, **347**, 164-167.