## Supplementary Materials

## A. Time-resolved Change of Transmittance

Figure S1 shows the normalised change of transmittance,  $\Delta T/T_0$ , as a function of the arrival time difference between the pump and probe pulses,  $\Delta t$ , on the sample surface. Here,  $T_0$  is the unexcited transmittance of pSi samples, and  $\Delta T = T_e - T_0$  with,  $T_e$  being the time-dependent transmittance of the samples after the excitation. From the figure, it can be concluded that the decay rate of  $\Delta T/T_0$  increases as a function of pSi porosity for all three types of samples. In addition, the decay function of  $\Delta T/T_0$  for the hydrogenated and oxidised samples are different — the former tends to decay linearly, while the latter decays exponentially. Besides, the recovery of the signal of oxidised samples is much faster than the hydrogenated ones. In the time window of measurements (550 ps), the signal of the oxidised samples completely recovered to the same level before the excitation for all samples with different porosities, while only 50% of the signal recovered for the hydrogenated sample with the highest porosity. After re-hydrogenation of the oxidised samples, the signal decay rates slowed down and reverted to a linear-like function similar to the hydrogenated samples. This indicates that the fast exponential decay results from the presence of oxygen passivation on the pore surface of pSi. The data presented on this figure was used to estimate the decay of the carrier density, N, shown in Fig. 2 of the main text.



FIG. S1. Normalised change of transmittance,  $\Delta T/T_0$ , as a function of the arrival time difference  $\Delta t$  between the pump and probe pulses for hydrogenated (a), oxidised (b) and re-hydrogenated (c) samples.

## B. Tauc Plot and Estimated Band-gap



FIG. S2. Tauc plots used to determine the band-gap of hydrogenated (a) and oxidised (b) pSi samples and the retrieved band-gap energies as a function of pSi porosity (c); Tauc plots used to determine the in-gap state energies of hydrogenated (d) and oxidised (e) pSi samples and the retrieved in-gap state energies as a function of pSi porosity (f).

A VIS-NIR spectrometer (see experimental approaches in the main article) was used to measure the transmittance, T, and reflectance, R, in order to obtain the absorptance, A = 1 - T - R. The band-gap energies were then retrieved from the Tauc plots as shown in Figure S2 (a)-(b), where the ordinate axis represents  $\sqrt{\alpha\omega}$  and the abscissa depicts the photon energy,  $\hbar\omega$ , with  $\alpha$  being the absorption coefficient calculated from the absorptance, A. By extrapolating the linear part of the curves in Figure S2 (a)-(b) to the abscissa, the band-gap energies are determined form the intercepts and plotted in Figure S2 (c), for both hydrogenated and oxidised samples as a function of pSi porosity. Besides, it can be noticed that, apart from the steep linear components which are associated with the energy-gap of samples, there also exist shallower linear components in the Tauc plots as extrapolated and shown in Figure S2 (d)-(e). These components indicate the existence of lower density in-gap states irregardless the surface passivation.

## C. Pathways of Auger Transition



FIG. S3. A possible *h*-*h*-*e* Auger transition in porous Si and the energy conservation conditions.  $E_g = E_c - E_v$  is the energy gap,  $\Delta E_{th}$  is the threshold energy.