Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Ultrafast carrier relaxation dynamics of photoexcited GaAs and GaAs/AlGaAs Nanowire Arrays

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1. Sample preparation process

The GaAs SNW array was grown by the Ga-assisted self-catalyzed method on Si (111) substrates by a DCA P600 solid source MBE system. [S1] The growth procedure is simply described as follows. The Si substrate was firstly dealt with ultrasonic cleaning in ethanol solution for 5 minutes and then etched with hydrofluoric acid. Secondly, the substrate is transferred into an MBE load-lock system to pre-degas at 200 °C for 2 h with pressure between 10^{-8} and 10^{-9} Torr. Thirdly, the substrate is sent to the MBE pretreatment chamber to degas for 2 h at 400 °C, and then it is transferred into the MBE growth chamber to degas again for 30 minutes at 750 °C. Finally, the growth progress is started. The GaAs nanowires was grown with Ga beam equivalent pressure (BEP) of 5.7×10^{-8} Torr and As BEP of 2.1×10^{-6} Torr. The V/III flux ratio is set to be 20.5. For the GaAs/AlGaAs core-shell SNWs, the GaAs-core growth process is the same to the bare GaAs SNWs. After the GaAs-cores grow for 30 minutes with the same BEPs of Ga and As, the Al flux is turned on with Al BEP of 4.3×10^{-8} Torr. After the AlGaAs-shells grown for 5 minutes at 800 °C, GaAs/AlGaAs core-shell SNWs are obtained.

2. Static spectroscopic characteristics

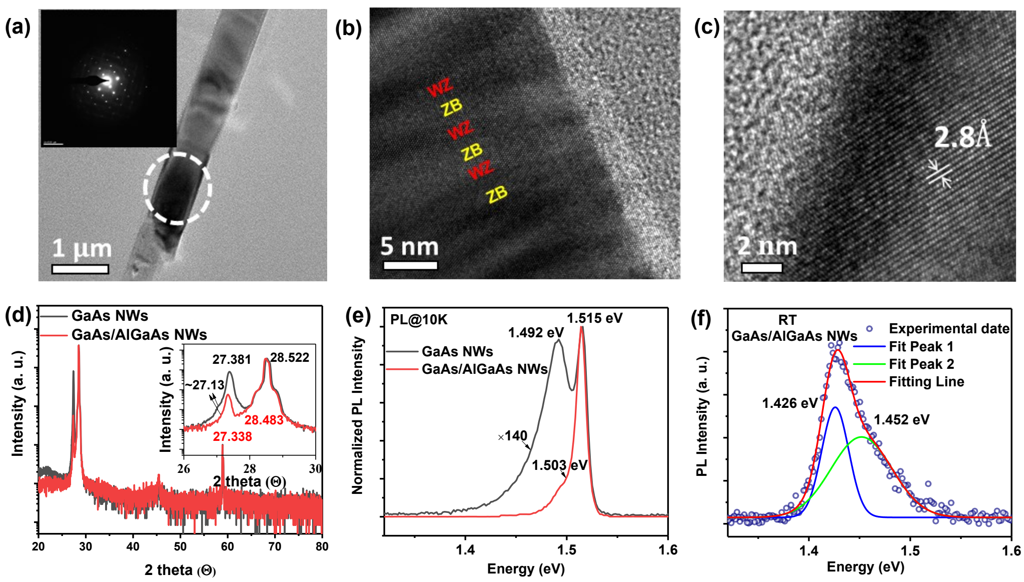

Fig. S1 (a–c) TEM and HRTEM of GaAs/AlGaAs SNWs. (d) XRD patterns of GaAs (black line) and GaAs/AlGaAs (red line) SNWs. (e) PL spectra of GaAs NWs (black line) and core-shell GaAs/AlGaAs SNWs (red line) at 10 K; (f) RT PL spectra and their Gaussian fitting lines of GaAs/AlGaAs NWs.

The TEM and HRTEM images of GaAs/AlGaAs NWs are shown in Fig. S1a–c. The SAED pattern (see inset of Fig.S1a) indicates that there are two sets of diffraction spots, which further confirm that there are two GaAs phases (WZ and ZB) in SNWs.[S2] In the HRTEM (Fig. S1b and c), the lattice distribution clearly shows that GaAs NWs consist of WZ and ZB segments.[S2] The lattice interplanar spacings are 2.8 Å, which is around the half of GaAs with lattice constant of 5.656 Å.[S3]

The X-ray diffraction (XRD) spectra of GaAs (black line) and core-shell GaAs/AlGaAs (red line) SNWs are shown in Fig. S1e. The narrow peak at 27.381° and the weak shoulder at ~27.13° are due to GaAs crystal with different phases, WZ GaAs (0002) and ZB GaAs (111), respectively.[S4, S5] The narrow GaAs peak becomes weaker and shifts slightly to lower angle after coating with AlGaAs shell. The peaks centered at a common position at 28.52° before and after AlGaAs-coating are ascribed to the reflection of Si (111) substrate. It can be seen that the bases of the common peaks are much broader than their tips. It is probably because the parasitic growth of SNWs, which leads to a highly defective and strained GaAs layer on Si substrate.[S2] No obvious new peaks appear after coating due to a high structural similarity and lattice-match between GaAs and AlGaAs.

Fig. S1f shows the PL spectra of GaAs and GaAs/AlGaAs SNW arrays at 10 K. For the PL of GaAs, two obvious peaks at 1.492 eV and 1.515 eV are originate from the surface defects states and band-to-band transition of ZB-type GaAs, respectively.[S4] For the PL of GaAs/AlGaAs, the two peaks are respectively due to ZB phase GaAs (1.515 eV) and WZ-ZB mixed phase (1.503 eV).[S4] Fig. S1g displays the PL of GaAs/AlGaAs at RT. Note that GaAs SNWs do not show any PL at RT. By fitting this profile with Gaussian function, two appreciable peaks are obtained at 1.426 eV and 1.452 eV. They are respectively originated from GaAs ZB and WZ phases, [S5] as further illustrated laser in Fig. S4.

3. Laser spectra and cross-correlation trace of pump and probe pulses

The pumps (800 nm and 650 nm) and broadband probe spectra in the experiment are shown in Fig. S2a. The time resolution of the experiment is measured by performing a second-order pump-probe intensity cross-correlation with a 10-μm-thick BBO crystal located at the sample position. The resultant cross-correlation trace yields a full-width at half-maximums (FWHMs) of ~80 fs (Figure S2b) and ~85 fs

(Figure S2c) for 800 nm and 650 nm pumps, respectively, with the broadband probe, corresponding to a time resolution of ~55-60 fs for a Gaussian pulse.

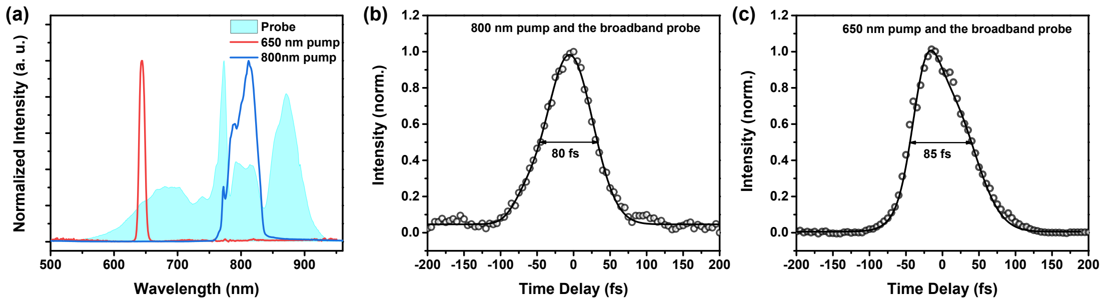

Fig. S2. (a) Pump (800 nm and 650 nm) and broadband probe spectra. (b) Cross-correlation trace (FWHM ~ 95 fs) of 800 nm pump and broadband probe pulses. (c) Cross-correlation trace (FWHM ~ 85 fs) of 650 nm pump and broadband probe pulses.

4. **Pump Fluence Dependence Measurements**

Pump fluence dependence measurements were performed to verify that photoexcitation occurs in the linear regime. Fig. S3 shows a log-log plot of the ΔA peak signal S obtained at the GaAs bandgap transition as a function of the pump fluence. Since $S \propto \alpha I^N$ (α is a constant), the slope of the log-log plot yields the photon order N. As shown in Fig. S3, the slopes of GaAs and GaAs/AlGaAs SNW arrays under 800 nm and 650 nm pumps are all quite close to 1. This confirms that the photoexcitation condition in our experiments occurs in a linear regime.

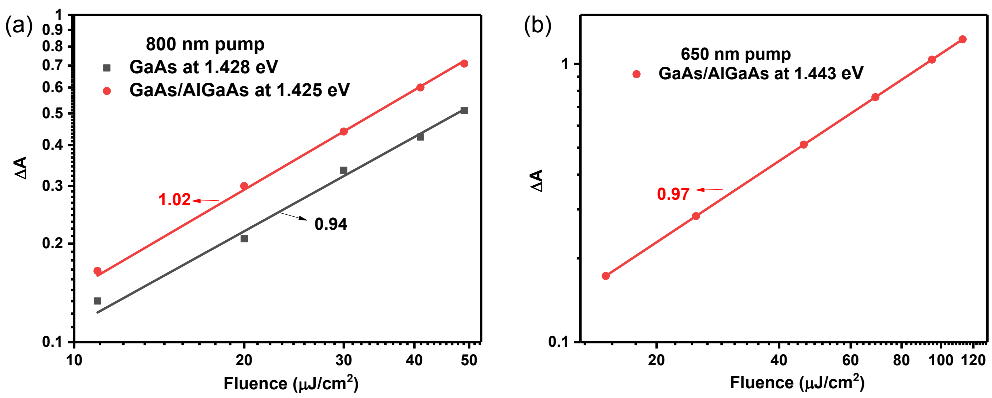

Fig. S3 Dependence of the maximum ΔA signal on the excitation pump fluence. The linear fit confirms that photoexcitation occurs via a one-photon process.

5. Variable-Temperature photoluminescence spectra of GaAs/AlGaAs nanowires.

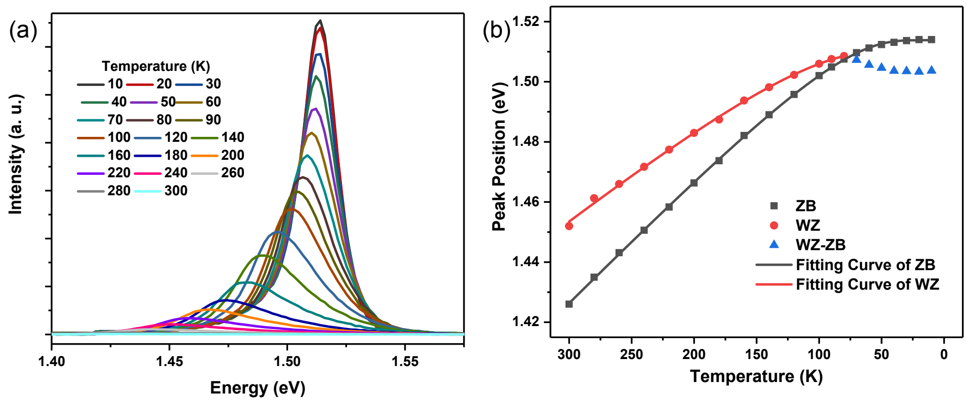

Fig. S4. (a) Temperature dependence PL spectra of GaAs/AlGaAs SNW arrays. (b) Variation of the PL peak positions with increasing sample temperatures.

Fig. S4a shows the temperature dependent PL spectra of GaAs/AlGaAs SNW arrays. The variation of the PL peak positions with increasing sample temperatures are shown in Fig. S4b. The two PL peaks are respectively due to GaAs ZB and WZ phases.[S6, S7] Both of them exhibit a blue-shift with increasing (decreasing) temperatures in the range of ~80–300 K, indicating that the band-gap of the sample decreases (increases) step by step because of the combination of lattice constriction and electron-phonon coupling. It should be noted that when the temperature is less than 80 K, the PL of the WZ phase disappears. A new PL source due to WZ-ZB mixed phase emerges[S6]. The plot of PL maxima as a function of temperature T (Figure S4b) can be fit to the semi-empirical function based on a semi-empirical Bose-Einstein expression, [S6]

$$E(T) = E_B - \alpha_B[1 + \frac{2}{\exp\left(\frac{\Theta}{T}\right) - 1}]$$

where E_B is a material-related parameter, a_B represents the strength of the electron–phonon interaction and Θ corresponds to the average phonon frequency. The fitting results give the paraments at 0K, including E_B≈1.561 eV, a_B≈0.047 eV, Θ≈220 K for ZB GaAs, and E_B≈1.564 eV, a_B≈0.053 eV, Θ≈316 K for WZ GaAs. From the PL peaks due to WZ and ZB phases, respectively, the energy gap WZ is around 20 meV larger than that of the ZB phase, in good agreement with the results previously reported. [S7]

Reference

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