Supporting Information for

# Decouple Electronic and Phononic Transport in Nanotwinned Structure: A New Strategy for Enhancing the Figure-of-merit of Thermoelectrics

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## I. The Calculation of Lorenz Number

The Wiedemann-Franz law shows the electrical thermal conductivity can be shown as

$$\kappa_e = L\sigma T,$$

(S1)

in which, $\sigma$ and $T$ are the electrical conductivity and temperature, respectively. $L$ is the Lorenz number and can be obtained

$$L = \left(\frac{k_b}{e}\right)^2 \left[\frac{3F_2}{F_0} - \left(\frac{2F_1}{F_0}\right)^2\right],$$

(S2)

with the reduced Fermi energy $\eta$, we have

$$F_i(\eta) = \int_0^\infty \frac{x^i}{e^{(x-\eta)}+1} dx,$$

(S3)

## II. The Computation of Effective Band Mass

In order to understand the mechanism that causes the improvement of the electrical conductivity, we calculate the effective band mass of the CBM, e.g., $\Gamma$ point and A point [Fig. 3]. It is well-known that for an external electrical field the effective mass of a charger carrier is defined as

$$\left(\frac{1}{m_b^*}\right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E_n(\mathbf{K})}{\partial K_i K_j}, i, j = x, y, z,$$

(S4)

where $i$ and $j$ indicate the reciprocal components, and $E_n(\mathbf{K})$ is the dispersion relation for the $n$-th band. Meanwhile, for group III-IV semiconductors, the energy $E_n(\mathbf{K})$ of the wave vector $\mathbf{K}$ at the band minimum or maximum can be written as

$$E(\mathbf{K}) = E_0 + \frac{\hbar^2}{2m_{b,x}^*} K_x^2 + \frac{\hbar^2}{2m_{b,y}^*} K_y^2 + \frac{\hbar^2}{2m_{b,z}^*} K_z^2.$$

(S5)

Combining Eq. (S1) and (S2), we have

$$
\left(\frac{1}{m_b^*}\right)_{ij} = \frac{1}{\mathsf{h}^2}
\begin{pmatrix}
\dfrac{\partial^2 E_n(\mathbf{K})}{\partial \mathrm{K}_x^2} & \dfrac{\partial^2 E_n(\mathbf{K})}{\partial \mathrm{K}_x \mathrm{K}_y} & \dfrac{\partial^2 E_n(\mathbf{K})}{\partial \mathrm{K}_x \mathrm{K}_z} \\[2mm]
\dfrac{\partial^2 E_n(\mathbf{K})}{\partial \mathrm{K}_y \mathrm{K}_x} & \dfrac{\partial^2 E_n(\mathbf{K})}{\partial \mathrm{K}_y^2} & \dfrac{\partial^2 E_n(\mathbf{K})}{\partial \mathrm{K}_y \mathrm{K}_z} \\[2mm]
\dfrac{\partial^2 E_n(\mathbf{K})}{\partial \mathrm{K}_z \mathrm{K}_x} & \dfrac{\partial^2 E_n(\mathbf{K})}{\partial \mathrm{K}_z \mathrm{K}_y} & \dfrac{\partial^2 E_n(\mathbf{K})}{\partial \mathrm{K}_z^2}
\end{pmatrix}. \tag{S6}
$$

Finally, the effective mass at the conduction band minima is calculated using finite difference method [https://github.com/afonari/emc].

### III. Electrical Transport Properties of Nanostructures

To calculate the electrical transport properties, the most popular method is adopted, which assumes the electronic band structure will be unchanged with doping and only the Fermi level is shifted. Then, following the electrical Boltzmann transport theory (BTE), the electrical conductivity ($\sigma$), electrical thermal conductivity ($\kappa_{el}$) and Seebeck coefficient ($S$) can be written as

$$
\sigma_{\alpha\beta}(T;\mu) = \frac{1}{\Omega}\int \Pi_{\alpha\beta}(\xi)\left[-\frac{\partial N_0^{F-D}(T;\mu)}{\partial \xi}\right]d\xi, \tag{S7}
$$

$$
\kappa_{\alpha\beta}^{el}(T;\mu) = \frac{1}{e^2 T\Omega}\int \Pi_{\alpha\beta}(\xi)(\xi-\mu)^2\left[-\frac{\partial N_0^{F-D}(T;\mu)}{\partial \xi}\right]d\xi, \tag{S8}
$$

$$
S_{\alpha\beta} = \frac{1}{eT\Omega\sigma_{\alpha\beta}(T;\mu)}\int \Pi_{\alpha\beta}(\xi)(\xi-\mu)\left[-\frac{\partial N_0^{F-D}(T;\mu)}{\partial \xi}\right]d\xi, \tag{S9}
$$

where $\alpha$ and $\beta$ are the Cartesian indices, $\Omega$, $e$, $\mu$, $T$ and $N_0^{F-D}$ are the volume of the unit cell, electron's charge, the Fermi level, the temperature and the Fermi-Dirac distribution

function, respectively. $\Pi_{\alpha\beta}(\xi)$ is the transport distribution function and can be written in the form of

$$\Pi_{\alpha\beta}(\xi) = \frac{1}{N}\sum_{i,\mathbf{K}} e^2 \tau_{total, membrane\ or\ bulk}^{el} v_\alpha(i,\mathbf{K}) v_\beta(i,\mathbf{K}) \left[ -\frac{\delta(\xi - \xi_{i,\mathbf{K}})}{d\xi} \right],$$ (S10)

where $N$ is the number of $\mathbf{K}$ points sampling, $i$, $v$ and $\tau_{total}^{el}$ are the band index, group velocity which can be calculated from the band structure and the relaxation time of electrons, respectively.

From the equations above, we can find the electron relaxation time is the key point to calculate the electrical transport properties. Here, the most popular way, that assumes the band structure of the grain is the same to the bulk counterpart [4, 5], is applied. Then, the electron relaxation time can be obtained by the Matthiessen's rule

$$\frac{1}{\tau_{tot, membrane}^{el}} = \frac{1}{\tau_{in}^{el}} + \frac{1}{\tau_{surf}^{el}} + \frac{1}{\tau_{GB}^{el}},$$ (S11)

and

$$\frac{1}{\tau_{tot, bulk-nanostructure}^{el}} = \frac{1}{\tau_{in}^{el}} + \frac{1}{\tau_{GB}^{el}},$$ (S12)

in which, $\tau_{in}^{el}$, $\tau_{surf}^{el}$ and $\tau_{GB}^{el}$ are the inherent electron, electron-surface and electron-grain boundary (GB) relaxation time, respectively. Here, in our calculations, the inherent electron relaxation time is obtained by fitting the experimental results (details can be found in SI Section V). The electron-surface or electron-GB relaxation time is computed via momentum dependent specularity $P(\mathbf{K})$ which considers the surface or grain boundary roughness by root mean square of roughness ($\Delta$). Therefore, we have

$$\tau_{surf}^{el}(\mathbf{K}) = \left[\frac{1+P_{surf}(\mathbf{K})}{1-P_{surf}(\mathbf{K})}\right]\frac{L}{v_{el}^{\perp}(\mathbf{K})}, \tag{S13}$$

$$\tau_{GB}^{el}(\mathbf{K}) = \left[\frac{1+P_{GB}(\mathbf{K})}{1-P_{GB}(\mathbf{K})}\right]\frac{D}{v_{el}^{\parallel}(\mathbf{K})\ or\ v_{el}(\mathbf{K})}, \tag{S14}$$

$$P(\mathbf{K},\nu) = \exp(-4\mathbf{K}^2\Delta^2\cos^2\phi) \tag{S15}$$

where $v_{el}^{\perp}(\mathbf{K})$ and $v_{el}^{\parallel}(\mathbf{K})$ are the component of electron group velocity normal and parallel to the surface, respectively. $\phi$ is the angle between the electron wave vector and the direction vector of the surface or GB. $L$ and $D$ are the thickness of the membrane and average size of grain. Finally, by averaging the relaxation time over all the reciprocal space, we can find

$$\tau_{surf}^{el} = \frac{\int \tau_{surf}^{el}(\mathbf{K})N_0^{F-D}\left[\xi(\mathbf{K})\right]d^3\mathbf{K}}{\int N_0^{F-D}\left[\xi(\mathbf{K})\right]d^3\mathbf{K}}. \tag{S16}$$

$$\tau_{GB}^{el} = \frac{\int \tau_{GB}^{el}(\mathbf{K})N_0^{F-D}\left[\xi(\mathbf{K})\right]d^3\mathbf{K}}{\int N_0^{F-D}\left[\xi(\mathbf{K})\right]d^3\mathbf{K}}. \tag{S17}$$

Then, the Seebeck coefficient, electrical thermal conductivity and power factor for the nanostructures can be obtained from Eqs. (S7)-(S9) and Eqs. (S13)-(S17). Here, all the nanomembranes in our paper have the (110) surfaces and the root mean square of the surface roughness is 0.125 nm, which is determined by various surfaces of Si NWs with different orientation (Fig. 5 in Ref. [6]). For the GB, we assume it is a very rough surface and will lead to $P(\mathbf{K},\nu) = 0$, which has been proved to be a quite good approximation (see results of Fig. 4 in our main text).

## IV. Theory to Calculate the Lattice Thermal Conductivity of Nanostructures

Solving phonon BTE by the relaxation time approximation [7], we can find the modal lattice thermal conductivity in the form of

$$\kappa_{ph}(\mathbf{K},\nu) = c_{ph}(\mathbf{K},\nu)\mathbf{v}_{ph}^2(\mathbf{K},\nu)\tau_{tot,membrane\,or\,bulk}^{ph}(\mathbf{K},\nu),$$

(S18)

where, $\mathbf{v}_{ph}(\mathbf{K},\nu)$ is the group velocity and can be obtained from lattice dynamics [8]. The volume specific heat $c_{ph}(\mathbf{K},\nu)$ can be calculated by $c_{ph}(\mathbf{K},\nu) = k_b/V$, in which $k_b$ and V is the Boltzmann constant and system volume, respectively. For the phonon relaxation time $\tau_{tot}^{ph}(\mathbf{K},\nu)$, it can be calculated using the Matthiessen's rule as well

$$\frac{1}{\tau_{tot,membrane}^{ph}(\mathbf{K},\nu)} = \frac{1}{\tau_{in}^{ph}(\mathbf{K},\nu)} + \frac{1}{\tau_{surf}^{ph}(\mathbf{K},\nu)} + \frac{1}{\tau_{GB}^{ph}(\mathbf{K},\nu)},$$

(S19)

and

$$\frac{1}{\tau_{tot,bulk}^{ph}(\mathbf{K},\nu)} = \frac{1}{\tau_{in}^{ph}(\mathbf{K},\nu)} + \frac{1}{\tau_{GB}^{ph}(\mathbf{K},\nu)},$$

(S20)

in which $\tau_{tot}^{ph}(\mathbf{K},\nu)$, $\tau_{in}^{ph}(\mathbf{K},\nu)$, $\tau_{surf}^{ph}(\mathbf{K},\nu)$ and $\tau_{GB}^{ph}(\mathbf{K},\nu)$ are the total relaxation time of a specific phonon, the inherent, phonon-surface and phonon-GB relaxation time, respectively. Here, the time domain normal mode analysis (TDNMA) [9, 10] is used to calculate the inherent phonon relaxation time $\tau_{in}^{ph}(\mathbf{K},\nu)$

$$\tau_{in}^{ph}(\mathbf{K},\nu) = \int_0^{t^*}\left(\frac{\langle E(\mathbf{K},\nu;t)E(\mathbf{K},\nu;0)\rangle}{\langle E(\mathbf{K},\nu;0)E(\mathbf{K},\nu;0)\rangle}\right)dt,$$

(S21)

where $t^*$ is the upper integration limit which should be much longer than the lifetime of the specific phonons. $E(\mathbf{K},\nu)$ is total energy of each phonon mode, and can be obtained by

$$E(\mathbf{K},\nu;t) = \frac{1}{2}\omega^2(\mathbf{K},\nu)X(\mathbf{K},\nu;t)X^*(\mathbf{K},\nu;t) + \frac{1}{2}\dot{X}(\mathbf{K},\nu;t)\dot{X}^*(\mathbf{K},\nu;t).$$

(S22)

in which, $X(\mathbf{K},\nu)$, $\dot{X}(\mathbf{K},\nu)$ and $\omega(\mathbf{K},\nu)$ are the normal mode coordinate, velocity and

frequency of phonon, respectively. More details about TDNMA can be found in Ref. [ 10].

The $\tau_{surf}^{ph}(\mathbf{K}, \nu)$ and $\tau_{GB}^{ph}(\mathbf{K}, \nu)$ are calculated by the similar method as electrons, and can be expressed as

$$\tau_{surf}^{ph}(\mathbf{K}, \nu) = \left[\frac{1 + P_{surf}(\mathbf{K})}{1 - P_{surf}(\mathbf{K})}\right] \frac{L}{v_{ph}^{\perp}(\mathbf{K}, \nu)}, \tag{S23}$$

$$\tau_{GB}^{ph}(\mathbf{K}, \nu) = \left[\frac{1 + P_{GB}(\mathbf{K})}{1 - P_{GB}(\mathbf{K})}\right] \frac{D}{v_{ph}^{\parallel}(\mathbf{K}, \nu) \ or \ v_{ph}(\mathbf{K}, \nu)}, \tag{S24}$$

in which, $v_{ph}^{\perp}(\mathbf{K}, \nu)$ and $v_{ph}^{\parallel}(\mathbf{K}, \nu)$ are the component of phonon group velocity $v_{ph}(\mathbf{K}, \nu)$ normal and parallel to the surface, respectively. Finally, combining Eqs. (S18)-(S20) and Eqs. (S21)-(S24), the lattice thermal conductivity of the Si-based nanostructures can be obtained.

## V.   Inherent Relaxation Time of Electrons

Here, to obtain the inherent electron relaxation time, we fit the experimental results rather than calculate it directly. It is easy to know the mobility of electrons in bulk Si [11, 12], then by applying

$$\langle \tau_{el} \rangle = \frac{\mu_0 m_b^*}{e}, \tag{S25}$$

in which, $\mu_0$, $m_b^*$ and $e$ are the mobility, average band effective mass and elementary charge of electrons, respectively. From the experimental results of Fig. S1, we can easily find that it is quite suitable to regard the inherent electron relaxation time as a constant for the carrier density ($1 \times 10^{18} - 1 \times 10^{20}$ cm$^{-3}$) considered in our paper.
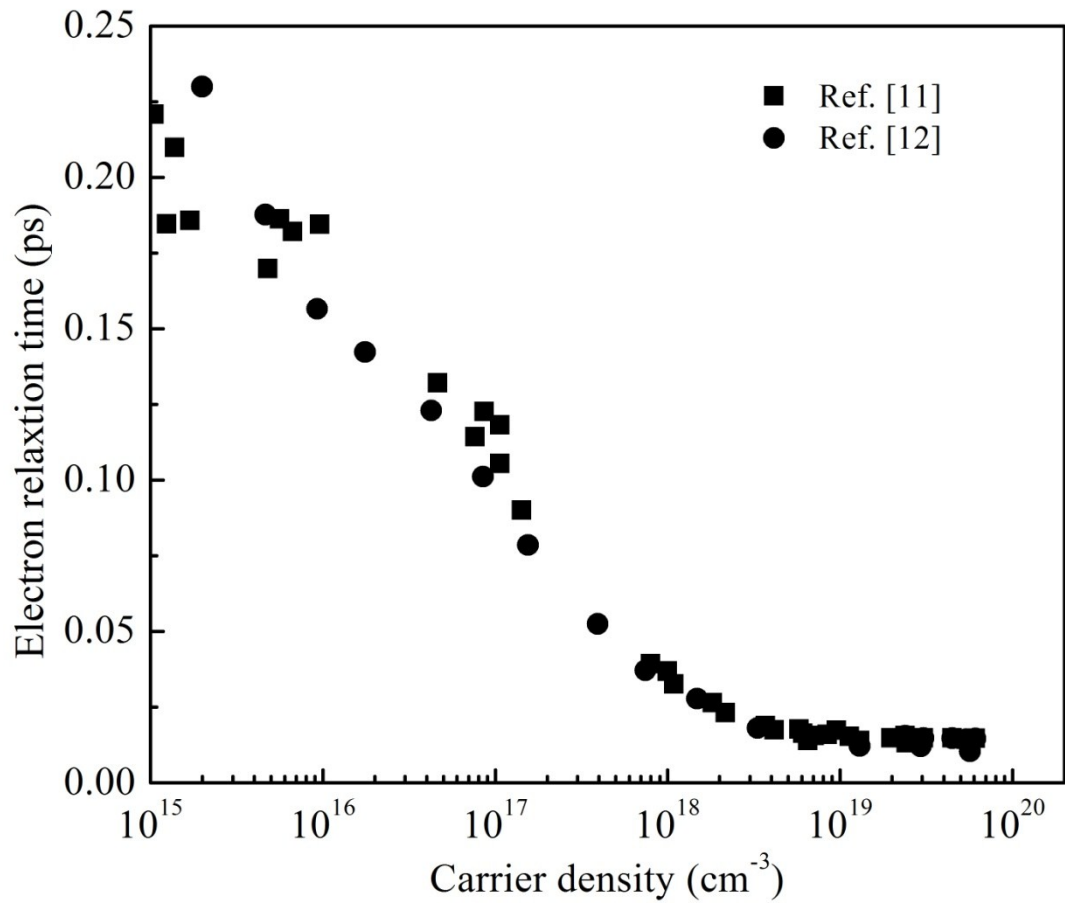
**Figure S1**. Inherent relaxation time of electrons in bulk Si measured by experiments.

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