

Structure and thermoelectric properties of spark plasma sintered ultrathin PbTe nanowires

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Supporting information

Carrier transport modeling

Our transport model is based on the linearized Boltzmann transport equation (BTE) with the relaxation time approximation. All the transport properties are expressed as integral functions of the differential conductivity $\sigma_d(E)$ over energy E defined by

$$\sigma_d(E) = e^2 \tau(E) v_x^2(E) \rho_{DOS}(E) \left(-\frac{\partial f_0(E)}{\partial E} \right), \quad (\text{S1})$$

where e is the electron charge, τ is the relaxation time, ρ_{DOS} is the density of states, v is the carrier velocity and f_0 is the Fermi-Dirac distribution. For multiple-band transport in PbTe, the transport properties are calculated in each of the bands with a relative position of the Fermi level E_F from the band edge and the contributions from each band are then added together to find the total

transport values in the bulk. The electrical conductivity σ , the Seebeck coefficient S , the Lorenz number L , and the electronic thermal conductivity κ_e are given, respectively, by

$$\sigma = \sum \int \sigma_d(E) dE, \quad (\text{S2})$$

$$S = \sum \left(\frac{k_B}{q} \right) \int \left[\frac{(E - E_F)}{k_B T} \right] \frac{\sigma_d(E)}{\sigma} dE, \quad (\text{S3})$$

$$L = \sum \frac{1}{\sigma} \left(\frac{k_B}{q} \right)^2 \int \left[\frac{E - E_F}{k_B T} \right]^2 \sigma_d(E) dE - S^2, \quad (\text{S4})$$

$$\kappa_e = L \sigma T, \quad (\text{S5})$$

where Σ is sum over the bands, q is $-e$ for conduction bands, and $+e$ for valence bands, T is the absolute temperature, and E_F is the relative position of the Fermi level to each of the band edges. (S5) is known as the Wiedemann-Franz relation.

For the transport modeling of p-type PbTe, both the L and Σ valence valleys are taken into account. As discussed in the main text, we chose 700 K as the band convergence temperature of the two valence valleys for better fitting of the experimental Seebeck coefficients. The conduction band at the L valley is also considered in the modeling, but it turns out that the contribution of electrons in the transport properties is much smaller than that of holes in all of the unintentionally p-type doped PbTe samples studied in this work.

According to our BTE calculations, the Lorenz number calculated by (S4) is much lower than the conventional value ($2.45 \times 10^{-8} \text{ W } \Omega^{-1} \text{ K}^{-2}$) for all the three samples. For sample SPS405, the Lorenz number steadily decreases from 1.44×10^{-8} to $1.37 \times 10^{-8} \text{ W } \Omega^{-1} \text{ K}^{-2}$ as temperature increases from 300 K to 400 K. For sample SPS450 and SPS500, the Lorenz number is almost constant to be $1.35 \sim 1.38 \times 10^{-8} \text{ W } \Omega^{-1} \text{ K}^{-2}$ over the temperature range.

The relaxation time is determined by several major scattering mechanisms in PbTe. Acoustic phonon deformation potential scattering, polar optical phonon scattering, and ionized impurity scattering are included in our calculations for bulk PbTe, although it turns out that the acoustic phonon deformation potential scattering is a predominant scattering mechanism. In our nanostructured PbTe, additional scattering mechanisms such as grain boundary and defect scatterings can be very strong and reduce the mobility quite significantly. We modeled this additional scattering using the short-range defect scattering and the ionized (long-range) impurity scattering mechanisms.

The energy-dependent scattering time by acoustic phonon deformation potential for a non-parabolic band is given by

$$\tau_{AC}(E) = \frac{\pi \hbar^4 C_l}{2^{1/2} (m_d^*)^{3/2} D_a^2 k_B T \sqrt{E + \alpha E^2} (1 + 2\alpha E)}, \quad (S6)$$

where C_l is the elastic constant, m_d^* is the density of states effective mass for a single valley, D_a is the acoustic phonon deformation potential, and α is the non-parabolicity.

The scattering time by ionized impurities (II) is given by

$$\tau_{II}(E) = \frac{16 \sqrt{2 m_d^*} \pi \epsilon_0^2 (E + \alpha E^2)^{3/2}}{N_{II} e^4 (1 + 2\alpha E)} \left[\ln(1 + \delta_0^{-1}) - \frac{\delta_0}{1 + \delta_0} \right]^{-1}, \quad (S7)$$

where N_{II} is the ionized impurity density, ϵ_∞ and ϵ_0 are the static permittivity values, and

$$\delta_0 = \hbar^2 / (8 m_d^* r_0^2 E). \quad r_0 \text{ is the screening length given by } 1/r_0^2 = (e^2 / \epsilon_0) \int_0^\infty (-\partial f_0 / \partial E) \rho_{DOS}(E) dE.$$

The scattering time by short-range deformation potential of defects is given by

$$\tau_{SD}(E) = \frac{\pi \hbar^4}{\sqrt{2} U_{SD}^2 (m_d^*)^{3/2} N_{SD} \sqrt{E + \alpha E^2} (1 + 2\alpha E)} \left[(1 - A)^2 - B \right]^{-1}, \quad (S8)$$

where $A = \alpha E(1 - K_{SD})/(1 + 2\alpha E)$, $B = 8\alpha E(1 + \alpha E)K_{SD}/3(1 + 2\alpha E)^2$, N_{SD} is the defect density, and K_{SD} is the ratio of the short range deformation potential coupling constants of valence and conduction band defects. The scattering parameters used for fitting of the transport properties of each sample are given in Table S-1.

With the assumption that the different scattering events are independent of each other, the total energy-dependent scattering time can be obtained by

$$\frac{1}{\tau(E)} = \frac{1}{\tau_{AC}(E)} + \frac{1}{\tau_{II}(E)} + \frac{1}{\tau_{SD}(E)}. \quad (S9)$$

This total scattering time is plugged into (S1) to calculate the differential conductivity as a function of energy, which is then used to calculate the thermoelectric properties of the nanostructured PbTe using (S2) through (S5).

TABLE S-1. Scattering parameters used for fitting of transport properties of the three PbTe samples

Sample	D_a (eV)	N_{II} (cm ⁻³)	U_{SD} (J/m ³)	N_{SD} (cm ⁻³)	K_{SD}
SPS405	32	1.4×10^{21}	2×10^{-46}	1×10^{20}	1.5
SPS450	32	4.2×10^{20}	2×10^{-46}	6×10^{19}	1.5
SPS500	32	4.4×10^{20}	2×10^{-46}	1.7×10^{20}	1.5