Electronic Supplementary Information

Synergy between defects, charge neutrality and energy filtering in hyper-doped nanocrystalline materials for high thermoelectric efficiency

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Transport model

The transport properties have been calculated using Boltzmann transport equation within the relaxation time approximation. The conductivity σ and the Seebeck coefficient S are respectively given in terms of the transport integrals K_s:

$$\sigma = e^2 K_1 \tag{S1}$$

$$S = -\frac{1}{eT}\left(E_F - \frac{K_2}{K_1}\right) \tag{S2}$$

where e is the carrier charge that is negative for electrons and positive for holes and E_F is the Fermi energy. The transport integrals can be written [S1]:

$$K_s = -\frac{4}{3m^*}\int_0^\infty N(E)\tau(E)E^s T(E)\frac{\partial f(E)}{\partial E}dE \tag{S3}$$

where $N(E)$, $\tau(E)$ and $f(E)$ are the density of states, the relaxation time and the fermi distribution function respectively. The electron/hole energy E is measured from the bottom/top of the conduction/valence band. The transmission coefficient $T(E)$ is to account for the presence of non-uniformity and expresses the probability for a carrier with energy E to participate to transport. In the energy filtering model, the transmission probability over an energy barrier V_b can be approximated by a step function:

$$T(E) = \begin{cases} 1 & E > V_b \\ 0 & E < V_b \end{cases} \quad \text{(S4)}$$

According to Equations (S3) and (S4), only carriers with energies E > V_b participate to transport. Analytical formalism can be derived for the dependence of the transport coefficients on V_b in the degenerate and non-degenerate transport regimes [S1]. The energy barrier provides energy filtering of mobile carriers resulting in decrease of the conductivity and enhancement of the Seebeck coefficient.

The relaxation time has been calculated using Matthiesen'rule and taking into account phonon scattering and impurity scattering as described in Section 2.2 of the main text.

Partial ionization of dopants

In a doped semiconductor, the concentration of ionized dopants and the concentration of free carriers are determined by the electrostatic charge neutrality condition $n + N_A^- = p + N_D^+$, where n and p denote the electron and the hole concentrations respectively. N_A^- is the ionized acceptor concentration. N_D^+ is the ionized donor concentration. N_D^+ is negligible in the p-doped samples and is omitted. The ionized acceptor concentration depends on temperature T and the acceptor activation energy E_A [S2]. The acceptor activation energy depends itself on the type of acceptors and the acceptor concentration [S2,S3]. For B in Si, it is ~45 meV for small N_A, decreasing with increasing N_A and practically vanishing for $N_A > 10^{18}$ cm^{-3}. The calculated hole concentration for B concentration 4×10^{20} cm^{-3} is shown in Figure S1 as a function of temperature.

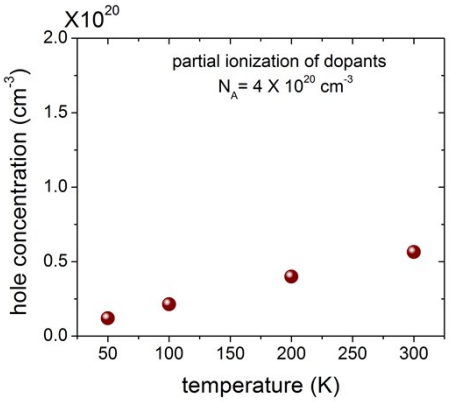

Figure S1. The hole concentration versus temperature for boron concentration N_A=4X10^{20}cm^{-3}.

Concentration of scatterers

The scatterers concentration has been estimated by fitting the measured mobility and is shown in Figure S2. Scatterers include defects and dopants.

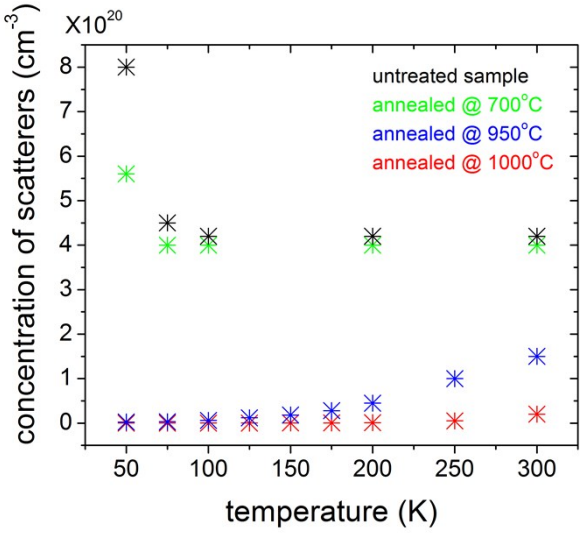

Figure S2. The estimated concentration of scatterers in the grains versus temperature for the four samples.

References

[S1] X. Zianni and D. Narducci, Journal of Applied Physics **117**, 035102 (2015)

[S2] Sheng S. Li, Solid State Electronics **21,** 1109 (1978)

[S3] T. F. Lee and T. C. McGill, Journal of Applied Physics **46**, 373 (1975)