Doping of thermoelectric PbSe with chemically inert secondary phase nanoparticles

Chao-Feng Wu, Heng Wang*, Qimin Yan, Tian-Ran Wei and Jing-Feng Li*

I. Micro-hard tests and Indentation morphologies

Figure S1. (a) Micro-hardness values as a function of SiC content, and indentation morphologies of (b) 0 vol% and 2 vol% samples.

II. XRD results and Microscopy images

Figure S2. (a) XRD results of PbSe-SiC composites and (b) enlarged area of (420) peaks.
III. Defect calculation results and embedded nanoparticle information.

Table S1. Some electronic information of embedded particles.$^{1,6}$

<table>
<thead>
<tr>
<th>particles</th>
<th>diameters</th>
<th>bandgap (300K)</th>
<th>W.F. (eV)</th>
<th>E.A. (eV)</th>
<th>$n_h$ cm$^{-3}$</th>
<th>surface condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC(6H)</td>
<td>40nm/60nm</td>
<td>3.02eV</td>
<td>4.89</td>
<td>3.7-3.8</td>
<td>1.1e20(n)</td>
<td>hydrophobic (HF, polished)</td>
</tr>
<tr>
<td>Si</td>
<td>1μm</td>
<td>1.17eV</td>
<td>4.15</td>
<td>4.05</td>
<td>-</td>
<td>hydrophobic (HF-treated)</td>
</tr>
<tr>
<td>C(diamond)</td>
<td>50nm</td>
<td>5.5eV</td>
<td>5.1</td>
<td>0.45-0.75</td>
<td>-</td>
<td>hydrophobic</td>
</tr>
<tr>
<td>C(graphite)</td>
<td>&gt;100μm</td>
<td>-</td>
<td>4.4-5.2</td>
<td>4.4-5.2</td>
<td>2e20(n)</td>
<td>hydrophobic</td>
</tr>
<tr>
<td>CNT</td>
<td>D15nm*1μm</td>
<td>-</td>
<td>-</td>
<td>4.4-5.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PbSe</td>
<td></td>
<td>0.27eV</td>
<td>4.6</td>
<td>4.21</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
IV. Scanning Kelvin Probe Force morphology (SKPM)

Figure S5. SKPM results of the 5 vol% sample, where a continuous change in surface potential was observed.

V. Co-doping results of Cl substitutes and SiC in PbSe

Figure S6. Hall carrier concentration of (a) 1 vol% and (b) 5 vol% samples with different Cl substitutes.

VI. Cycled tests of PbSe + 5 vol % SiC composition
VII. Discussions on the boundary scattering in MAed PbSe and PbSe-SiC composite

For conventional \( n \)-type PbSe synthesized by melting and hot-pressing (Fig. 4(b) and 4(c), blue triangles), the carrier mobility can be well described using acoustic phonon scattering with a deformation potential coefficient (\( \Xi \)) of 25 eV.

The mobility of PbSe made with mechanical alloying (Fig. 5) are always lower than that of melted ones. Obviously high density of defects and grain boundaries caused carrier scattering. We treat grain boundaries and defects (mainly dislocations) as perturbations (due to their narrow potential barriers) to the periodic lattice potential, and call this aspect of their influence “interface scattering”. “Interface” here includes grain boundaries, dislocations and interfaces. The scattering probability is independent of electron wave vector \( k \). We write the relaxation time due to interface scattering (under the frame work of Kane band model) as:

\[
\tau_{\text{int}} = \frac{\pi \hbar^4}{(2m_e)^{3/2} (k_B T)^{1/2} \Omega U_{\text{int}}^2 x_{\text{int}}^2} e^{-1/2} (1 + \varepsilon \alpha)^{-1/2} (1 + 2\varepsilon \alpha)^{-1}
\]
here $h$ is the reduced plank constant, $m^*$ the band effective mass, $k_B$ the Boltzmann constant, $T$ the absolute temperature, $\Omega$ the volume per unit cell of the matrix, $U_{\text{int}}$ the scattering parameter, $x_{\text{int}}$ the average number of interfaces in one unit cell, $\epsilon$ the reduced carrier energy and $\alpha = k_B T / E_g$ ($E_g$ is the gap between conduction and valence band).

The scattering parameter $U_{\text{int}}$ (in unit of eV) determines the magnitude of $\tau_{\text{int}}$. Qualitatively, $U_{\text{int}}$ should be related to the interface potential barrier height, and $x_{\text{int}}$ represents the probability of carriers encountering one interface within a unit cell. Estimating “$x_{\text{int}}$” and the interface concentration is out of scope of this paper, thus $x_{\text{int}} U_{\text{int}}^2$ is treated here as a fitting parameter independent of carrier energy and temperature. We found this describing experimental mobilities at different temperatures very well (Fig. 4(b), Fig. 4(c) and Fig. S8). With a fitted value of $\sim$0.032 (eV)$^2$ for $x_{\text{int}} U_{\text{int}}^2$. If we assume $x_{\text{int}}$ takes values from 0.01 to 0.1% (correspond to interface density 4E19 to 4E18 cm$^{-3}$), $U_{\text{int}}$ would have values from 1.8 eV to 5.7 eV.

Figure S8. Mobility simulation at different temperatures for general MAed samples.
For the samples with SiC, the mobility are found even lower. Embedded SiC nanoparticles bring additional interfaces and defects. Consider the particle sizes (~100 nm) are much greater than electron wavelength (1 to 10 nm) we treat the scattering from SiC nanoparticles largely the same way as above:

\[
\tau_{\text{SiC}} = \frac{\pi \hbar^4}{(2m_e)^{3/2} (k_b T)^{1/2} \Omega U_{b}^2 x_{\text{SiC}}} \varepsilon^{-1/2} (1 + \varepsilon\alpha)^{-1/2} (1 + 2\varepsilon\alpha)^{-1}
\]

The scattering parameter \(U_{b}'\) is due to PbSe-SiC interfaces, and this value is determined through fitting, which explained mobilities measured in PbSe with SiC (Fig. S9).

![Figure S9. Mobility simulation at different temperatures for PbSe-SiC samples.](image)

Besides, the SiC volume fraction is further linked to electron density through an empirical relation (Fig. S10):

\[
n_{H} \times 10^{19} \text{ cm}^{-3} = A \times x^{1/3}
\]
where $A$ is constant pre-factor. We mark here that the PbSe-SiC interface is believed to be the source of free carriers and should contain a high density of ionized defects, which would cause scattering of the carriers as well. We didn’t take into account this here due to the lack of theoretical models, in addition, the high dielectric constant in lead chalcogenides would reduce the magnitude of such scattering through screening.

![Figure S10. An empirical relation between $n_{\text{H}}$ and SiC volume fraction ($x$) for PbSe-SiC.](image)

References