Valleytronics of III–V solid solutions for thermoelectric application

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It is shown that the degeneracy of the bandstructure has different impacts on thermoelectric properties of III–V materials. A comprehensive list of III–V solid solution alloys that can make multi-valley bandstructures is presented and the transport parameters affecting their thermoelectric power factor are discussed. It is shown that in some cases, such as GaInP ternary alloy, the power factor is enhanced significantly near the valley convergence point, but in some other cases, such as AlGaAs, the enhancement is marginal and away from the valley convergence point. Therefore, in addition to the bandstructure engineering, detailed calculation of the transport parameters is also required to determine the optimum alloy composition that can improve the thermoelectric properties.
near the transition point; hence, for a given carrier concentration, the Fermi energy reduces, which results in the enhancement of Seebeck coefficient. If this enhancement happens without loss of the electrical conductivity, the thermoelectric power factor increases. To reach our goal, the alloy must satisfy two conditions: (a) the composition should be adjusted so that the different valleys converge. In the case of solid solution, the volume fraction is simply the “knob” for tuning the energy of the valleys and fulfilling the condition; (b) the conduction band minimum of material 1 (CBM1) should be at a different wavenumber than that of material 2 (CBM2) so that the band crossing happens. The later condition is required only if the bowing factor of the resulted bandstructure is negligible and the bands do not cross. For example, Fig. 1 shows the schematics of the bandstructure with conduction band minima at L, Γ, and X (panel a) and the band-gap energies (EΓ, EL, and EX) as a function of the x-composition parameter for GaIn1−xP (panel b). The arrows in panel (a) indicate the intervalley electron scattering among different valleys.

In this ternary alloy, the conduction band minimum makes transition from Γ to L point at x ≈ 0.67 and again from L to X point at x ≈ 0.77 as the Ga concentration increases from zero to one. Therefore, the band degeneracy at x ≈ 0.67 is five-fold and at x ≈ 0.77 is 7-fold. The latter is even larger than the degeneracy of the conduction band in some of the good thermoelectric materials like Bi2Te3 and SiGe (both 6-fold degenerate). It is worth noting that EΓ value at x ≈ 0.77 is very close to EL and EX. Therefore, at temperatures that kBT is comparable to or larger than the energy difference, the Γ valley also contributes in the carrier transport, adding to the X and L contributions, which would further enhance the Seebeck coefficient.

We calculated the main thermoelectric properties of n type GaIn1−xP by solving the Boltzmann Transport Equation. For the model calculations, we followed the methodologies discussed in our previous works. The calculation details as well as the model validations by the experimental data are presented in the supplementary material available in the online version of this article. The calculation was performed for fixed doping concentration of N = 1.5 × 1020 cm−3 at T = 600 °C. This value of N maximizes the zT at the optimum x. As shown in Fig. 2, the relatively large value of the degeneracy of the band in this material system has resulted in significant enhancement of the Seebeck coefficient. The peak power factor occurs at x ≈ 0.7, which is near both the Γ–L and L–X band convergence points. At this range of composition, Γ, L and X valleys are near each other (within a kBT). Therefore, there are effectively 8 carrier pockets at the band edge. When the Γ, L, and X are within several kBT from each other, the carriers can populate all the valleys and contribute in electronic transport. The electrical and thermal transport properties are calculated and shown in Fig. 2. In order to show the effect of the intervalley scattering, we have plotted the values corresponding to two case of with or without the inclusion of the intervalley scattering. Alloying of InP with Ga reduces the electron mobility; however, the effect in Seebeck coefficient is stronger and results in significant enhancement of the power factor, as shown in Fig. 2a and b. Our calculations also show that the multi-band transport has significantly reduced the thermal conductivity, which is mainly due to the reduction of the electronic part of the thermal conduction (the thermal conductivity components are not shown in the plot). Therefore, the combination of the two mechanisms predicts a high zT close to 1.1 near x ≈ 0.74.

In contrast to GaIn1−xP material system, our calculations for n type AlGa1−xP material system, our calculations for n type AlGa1−x shows that the optimum bandstructure, i.e., where the zT is maximized, deviates from the valley convergence point. The calculated thermoelectric properties for AlGa1−x as versus x at 600 °C is shown in Fig. 3. The doping concentration was fixed at N = 1.05 × 1019 cm−3, which maximizes the zT at optimum x.

In this case, the band extrema L and X converge at x ≈ 0.42. It is generally expected that the zT should increase near this point. However, model calculations predict that zT reaches a peak at x ≈ 15% and it reduces significantly as x approaches 0.42. This different trend indicates that the bands convergence is not necessarily the optimum place at which zT is enhanced. The main reason for the zT reduction near the valley convergence point is due to the significant drop of the electrical conductivity near this point (Fig. 3a). In general, the valley convergence affects the transport properties in two ways. First, it enhances the density of states; hence, improves the Seebeck coefficient. Second, it increases the intervalley charge carrier scattering, which reduces both the electrical conductivity and the Seebeck coefficient. The dominant scattering near the

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**Fig. 1** (a) Illustration of a multivalley band structure with valleys L, Γ, and X. (b) Conduction band minima vs. x for GaIn1−xP. The power factor is calculated for doping concentration of 1.5 × 1020 cm−3 at 600 °C. Symbols represent the experimental data.
intervalley scattering it has a peak at $zT = 0.8$ at $x = 0.55$ if the inter-valley scattering is removed, and it shows a significant drop upon inclusion of the intervalley scattering and the peak value is $zT \approx 0.27$ at $x = 0.16$.

A comprehensive list of III–V solid-solution candidates for thermoelectric application is presented in Table 1. The band parameters were collected from ref. 37 and the valley convergence was calculated using Vegard’s law by the inclusion of the bowing parameters whenever the data was available. The table shows the candid binary solid solution $A_{x}B_{1-x}$, the lattice constant mismatch $\Delta a$, the bandgap $E_g$ and the corresponding band-edge for material A and B, the composition $x$, where the bands meet and its corresponding degeneracy $N_\text{v}$ and the valleys, the composition $x$ which has the highest number of carrier pockets near the band-edge and the corresponding degeneracy $N_\text{v}$, and the overlap temperature $T_o$. As an example, for the case of GaP-GaSb, i.e. (GaP)$_{1-x}$(GaSb)$_{x}$, the lattice mismatch is %11.8. The bandgap for GaP and GaSb are 2.35 eV at $X$ point and 0.81 eV at $I$ point, respectively.$X$ and $L$ valleys meet at $x = 0.42$ resulting in 7 fold degeneracy. At $x \sim 0.38$ and at $T > 140$ K, $I$ point becomes less than $2k_BT$ above the $X$ and $L$ points. Therefore, at $T > 150$ K, the $I$ point becomes also populated and there will be 8 carrier pockets contributing in transport. The materials in the non-shaded rows are suggested as good candidates due to their high degeneracy of the band at the valley convergence point. For the first nine rows, at temperatures above $T_o$, the $I$, $X$ and $L$ CBMs will all contribute in transport due to the broadening of the Fermi–Dirac distribution. This contribution in turn increases the number of carrier pockets near the Fermi energy. Interestingly, for GaP-GaSb, GaP-InP, InAs-AlAs, GaSb-AIP, and GaAs-AlAs the overlapping temperature is below the room temperature.

The valley convergence can occur between any two valleys of $I$, $X$, and $L$. In such cases, $x$ composition corresponds to the valley convergence that results in highest degeneracy. The overlap temperature $T_o$ refers to the temperature above which the energy separation of the three valleys of $I$, $X$, and $L$ becomes less than $2k_BT$.
Table 1 List of investigated III–V solid solution alloys

<table>
<thead>
<tr>
<th>A₁BₓC₁</th>
<th>Δa</th>
<th>Eₜ (eV)</th>
<th>x₁Nₓ₁</th>
<th>x₂Nₓ₂</th>
<th>Tᵣ (K)</th>
</tr>
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<tbody>
<tr>
<td>Ga₃PₓGaSb</td>
<td>0.1</td>
<td>(0.25x)</td>
<td>0.42</td>
<td>0.38</td>
<td>140</td>
</tr>
<tr>
<td>Ga₃PₓInP</td>
<td>0.1</td>
<td>(0.25x)</td>
<td>0.72</td>
<td>0.70</td>
<td>125</td>
</tr>
<tr>
<td>InAsₓAl₁₋ₓAs</td>
<td>0.6</td>
<td>(0.47x)</td>
<td>0.37</td>
<td>0.37</td>
<td>161</td>
</tr>
<tr>
<td>GaSbₓA₁₋ₓP</td>
<td>0.1</td>
<td>(0.81x)</td>
<td>0.77</td>
<td>0.77</td>
<td>202</td>
</tr>
<tr>
<td>InAsₓAl₁₋ₓAs</td>
<td>0.18</td>
<td>(1.21x)</td>
<td>0.58</td>
<td>0.58</td>
<td>48</td>
</tr>
<tr>
<td>GaSbₓIn₁₋ₓP</td>
<td>0.6</td>
<td>(1.21x)</td>
<td>0.60</td>
<td>0.60</td>
<td>897</td>
</tr>
<tr>
<td>Ga₃PₓGa₁₋ₓAs</td>
<td>0.35</td>
<td>(1.51x)</td>
<td>0.45</td>
<td>0.45</td>
<td>554</td>
</tr>
<tr>
<td>GaSbₓIn₁₋ₓP</td>
<td>0.6</td>
<td>(0.81x)</td>
<td>0.53</td>
<td>0.67</td>
<td>487</td>
</tr>
<tr>
<td>Ga₃PₓIn₁₋ₓP</td>
<td>0.11</td>
<td>(0.35x)</td>
<td>0.65</td>
<td>0.65</td>
<td>805</td>
</tr>
<tr>
<td>InSbₓAsₓSb</td>
<td>0.55</td>
<td>(0.24x)</td>
<td>0.54</td>
<td>-</td>
<td>2636</td>
</tr>
<tr>
<td>InAsₓSbₓSb</td>
<td>0.12</td>
<td>(0.42x)</td>
<td>0.40</td>
<td>-</td>
<td>1485</td>
</tr>
<tr>
<td>InPₓA₁₋ₓP</td>
<td>0.7</td>
<td>(1.42x)</td>
<td>0.62</td>
<td>-</td>
<td>2336</td>
</tr>
<tr>
<td>Ga₃PₓAs₁₋ₓSb</td>
<td>0.38</td>
<td>(2.35x)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ga₃PₓAl₁₋ₓP</td>
<td>0.1</td>
<td>(2.35x)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ga₃PₓAl₁₋ₓA₁₋ₓSb</td>
<td>0.37</td>
<td>(2.35x)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ga₃PₓIn₁₋ₓP</td>
<td>0.37</td>
<td>(1.52x)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al₁₋ₓSbₓSb</td>
<td>0.8</td>
<td>(2.24x)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al₁₋ₓPₓSb</td>
<td>0.11</td>
<td>(2.52x)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al₁₋ₓPₓA₁₋ₓSb</td>
<td>0.36</td>
<td>(2.52x)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Δa: the lattice mismatch. Eₜ: band gap. The corresponding valley is also shown. x₁ and Nₓ₁: the composition where two valleys meet and the corresponding valley degeneracy. x₂ and Nₓ₂: the composition with highest number of contributing electron pockets in transport at temperatures above Tᵣ and the corresponding number of carrier pockets. Tᵣ: the temperature above which L, X, and Γ valleys can be populated at optimum Fermi energy. The band parameter data is taken from Vurgaftman et al. 15

Therefore, all the three bands, Γ, L, and X contribute effectively in the transport. It is also worth mentioning that the mentioned materials have zinc blende structure, and except Ga₃PₓGaSb and Ga₃PₓInP, the valley convergence occurs at X/L cross point. Ga₃PₓGaSb and Ga₃PₓInP are especially interesting as they have the highest degeneracy at x₁. The convergence of X and L valleys at CBM in these two solid solutions is due to their large bandstructure bowing parameters. 27 For the three alloys in the lightly shaded area of the table, there is no X/L valley convergence and the overlap temperature is above the melting point. For the remaining seven alloys in the darkly shaded area, there is neither X/L nor X/L valley convergence.

As discussed earlier, the high degeneracy of the band is only one of the criteria for a good thermoelectric material. The non-dominance of the inter-valley scattering must be also satisfied in order to observe the improvement of the thermoelectric power factor by multi-valley transport conduction. If the inter-valley scattering becomes significant near the valley convergence point, the optimum alloy composition can deviate away from this point or the zT may be reduced. For example, as shown in Fig. 3, the optimum x parameter for n-type AlₓGa₁₋ₓAs deviates from where the valleys meet each other (x = 0.42) and happens at x = 0.16. Therefore, the compositions listed in.

Table 1 does not necessarily maximize the power factor.

In summary, it was shown that valleytronics has different impacts on thermoelectric properties of III–V alloys. A comprehensive list of materials that can make a continuous solid solution with high valley degeneracy were identified. The continuous solid solution of these alloys provide means for tuning the valley characteristics of the band structure. The solid solution of two materials having band minima with dissimilar wavenumbers allows convergence of the valleys and enhancing the valley degeneracy (Nₓ), hence, the electronic density of states. The enhancement of the density of states generally improves the Seebeck coefficient providing a roadmap for engineering high performance thermoelectric materials. However, it was also discussed that the enhancement of the density of state may be accompanied by large intervalley scattering that can deviate the optimum alloy composition away from the valley convergence point or reduce the zT. Therefore, as the next step, the transport calculations are required for the valleytronics of these candid alloys in the search for good thermoelectric materials.

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