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Energy Filtering and Thermoelectrics: Artifact or Artifice?

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The possibility of selecting carrier energies by using suitable potential barriers has played a long-standing role in the physics of thermionic devices. It entered instead the arena of thermoelectricity only in the Nineties through the pioneering work of Rowe and Min and of Nishio and Hirano. Since then, the virtuous use of energy barrier in thermoelectricity has gone through alternating fortunes, with analyses sustaining its capacity as a tool to decouple the adverse interdependency between Seebeck coefficient and electrical conductivity; and papers disproving instead such a possibility. In spite of a yet uncomplete theoretical framework, over the last years an impressive number of papers has been published reporting unusual dependencies of thermopower and conductivity upon carrier densities, mostly in nanocomposites—and attributing them to energy filtering. Aim of this paper is to discuss to which extent and under which physical constraints energy filtering may be actually invoked to explain enhanced power factors—and which alternate possibilities of explanation may be considered instead.

Keywords: Energy Filtering, Thermoelectric Figure of Merit, Transport Phenomena, Scattering.

1. INTRODUCTION

In spite of a still not fully clear theoretical framework, the concept of energy filtering has found wide application in thermoelectricity. This is mostly related to the extended use of composites that, while initially motivated by the attempt of lowering the thermal conductivity, was then found sometimes beneficial also to enhance the material power factor $PF \equiv \sigma \alpha^2$ (where σ is the electrical conductivity and α is the Seebeck coefficient). Experimental literature has ranged from tellurides[1–3] to silicon and silicon alloys[4–7] but energy filtering has been invoked also for polymeric and carbon-based materials.[8, 9]

This paper will discuss to what extent experimental evidence of anomalous dependencies of the power factor on the carrier density may be compatible with the energy filtering effect. It will be shown that energy filtering may actually be a proper expediency to improve the thermoelectric figure of merit $ZT \equiv (PF/\kappa)T$ (where κ is the thermal conductivity and T is the absolute temperature). Yet, it will be also remarked that only in some experimental systems may energy filtering be appropriately invoked as the actual key factor explaining enhanced thermoelectric efficiency, with other effects possibly better explaining high power factors.

2. THEORY

2.1. Background

To the best of my knowledge the very first reference to the concept of energy filtering in thermoelectrics was in a 1995 paper by Rowe and Min,[10] where they analyzed the effect of multiple barriers on the Seebeck coefficient and on the electrical conductivity. Within the relaxation-time approximation they could show that the presence of adequately high barriers would have prevented bipolar effects, since minority carrier flow would be impeded. Such an effect was predicted to overcompensate the reduction of the electrical conductivity due to the decrease of flowing majority carriers. No analysis of the optimal spacing between barriers was however presented, that will be shown to play a major role in energy filtering. The first attempt to theoretically analyze the physics of the phenomenon dates a few years later and was due to Whitlow and Hirano.[11] Whitlow and Hirano extended the standard approach to cold electron filtering used in solid-state thermionics by considering the effect of a potential barrier E_b on the carrier spectral density $n(E)$, validating their model in a superlattice. Comparison of transport properties parallel ($\parallel$) and normal ($\perp$) to the multilayer was used to display the impact of energy filtering. In a simplified picture it could be shown that, since the spectral electrical

conductivity $\sigma'_\perp(E, E_b)$ equals its bulk value $\sigma'(E, 0)$ for $E \geq E_b$ while it is zero otherwise, the macroscopic conductivity $\sigma_\perp(E_b)$ may be predicted to reach a maximum value at an optimal E_b, while the Seebeck coefficient α monotonically increases with E_b. As expected, energy filtering in more effective at low temperatures, and both transport coefficients converge to their bulk (unfiltered) value in the high temperature limit. This analysis was perfected in a subsequent paper,[12] where the optimal barrier energy E_b^* was quantified to $E_F - q\alpha T$ (where E_F is the Fermi energy and $-q$ is the electron charge). Also, barrier width was shown to matter. Inter-barrier spacing d should largely exceed carrier momentum relaxation length λ_p (to enable their equilibration to the lattice, namely to guarantee a diffusive regime) but should be smaller than the energy relaxation length λ_E (to prevent carrier relaxation between two barriers).

The critical issue of momentum conservation was further analyzed by Bowers, Shakouri, and Gossard.[13] Referring once again to a superlattice, it was noted that only if transverse momentum $k_\perp$ is not conserved (i.e., if inelastic scattering occurs) is the lateral momentum conservation relaxed, so that the number of hot carriers overcoming the barrier is enhanced. Thus, the reduction of the conductivity is alleviated while α still profits of the reduction of carrier density. This implies that energy filtering is paradoxically more effective when non-planar barriers (e.g., ruggedized interfaces) are opposed to the electron flow as rough surfaces relax constraints on momentum conservation. A general expression of the optimal cutoff energy in the k-non-conservative case was put forward, that depends on the scattering mechanism(s) and on the effective mass of the relevant carrier.[14]

A radically different view of the energy filtering and of its possible use to enhance the PF was provided by Heiliger. His analysis focused on potential barriers at grain boundaries in polycrystalline heavily doped semiconductors.[15] Heiliger's model explicitly accounted for the relationship between E_b and E_F in homogeneous semiconductors. Using non-equilibrium Green's function he showed that when intergrain transport is ballistic (while intragrain transport is diffusive) the effective screening of the Coulomb potential at grain boundaries leads to barrier heights and widths too small for electrons to be significantly filtered.

Overall, it is apparent how the theoretical framework about energy filtering is far from being fully settled. In what follows no attempt will be made to reconcile different viewpoints. Instead, this contribution will be aimed at showing that simple qualitative (or semi-quantitative) reasoning may lead to exclude energy filtering as the process responsible for enhanced thermoelectric efficiency. In this sense it will be shown why invoking energy filtering as the only possible frame within which anomalously large power factors may be explained turns an artifact, namely the results of engineering potential landscapes within solids, into a mere rhetorical artifice. Instead, at least in nanocomposites much simpler phenomena may be invoked to explain enhanced power factors.

It might be worthwhile to stress that the wording 'energy filtering' is often used in physics with a completely different meaning, relating to Fabry–Perot resonance.[16] Although the naming is appropriate, this type of filtering, which requires a periodic sequence of barriers, would be non-beneficial to the power factor as it would completely prevent carrier flow away from resonance.

2.2. Energy Filtering in One-Phase Systems

Among others, Zianni and Neophytou analyzed in a series of papers how energy filtering should improve the power factor depending on the barrier height and the Fermi energy in single-phase systems and nanocomposites.[5, 17–19] In the relaxation-time approximation it may be shown[17] that in n-type semiconductors both σ and α can be written using the transport integrals K_s:

$$K_s = -\frac{4}{3m^*} \int_0^\infty g(E)\tau(E)E^s \partial_E f(E, E_F)\, dE \qquad (1)$$

where m^* is the effective mass of the majority carrier, $g(E)$ is the density of electronic states (DOS), $\tau(E)$ is the relaxation time, $f(E, E_F)$ is the Fermi–Dirac distribution function, E_F is the Fermi energy, and all energies are measured from the bottom of the conduction band (top of the valence band) for n-type (p-type) semiconductors. Thus

$$\sigma = q^2 K_1 \qquad (2)$$

(where $-q$ is the electron charge) and

$$\alpha = -\frac{1}{qT}\left(E_F - \frac{K_2}{K_1}\right) \qquad (3)$$

Therefore

$$\mathrm{PF} = \frac{K_1}{T^2}\left(E_F - \frac{K_2}{K_1}\right)^2 \qquad (4)$$

The density of states and the relaxation times are taken to depend upon E as $g(E) = g_0 E^r$ and $\tau(E) = \tau_0 E^p$ (where g_0, r, τ_0, and p are parameters not depending on E). In the presence of potential barriers of height E_b Eq. (1) may be written as

$$K_s(a, x_b, \eta_F) = -\frac{4g_0\tau_0}{3m^*}(k_B T)^{(a+s)-1}$$
$$\times \int_{x_b}^\infty x^{(a+s)-1}\partial_E f(E, E_F)\, dx \qquad (5)$$

where k_B is the Boltzmann constant, $a = p + r + 1$, $x = E/(k_B T)$, $\eta_F = E_F/(k_B T)$, and $x_b = E_b/(k_B T)$. For bulk semiconductors (single band, parabolic) $r = 1/2$ so that $a = p + 3/2$. As an example, in degenerate semiconductors

scattering is dominated by highly screened ionized impurities. Thus[20]

$$\frac{1}{\tau} = \frac{\pi N_D}{\hbar}\left(\frac{q^2 L_d^2}{\epsilon_s}\right)^2 g_C(E) \quad (6)$$

where $\hbar$ is the reduced Planck constant, N_D is the donor density (assumed to be the only heteroatom in the semiconductor), $g_C(E)$ is the conduction band DOS, ϵ_s is the semiconductor permittivity, and the screening length L_d may be written as[21]

$$L_d^{-2} = \frac{q^2 N_D}{\epsilon_s(k_B T)}\frac{F_{-1/2}(\eta_F)}{e^{\eta_F}} \quad (7)$$

where $F_j(\eta_F)$ is the Fermi-Dirac integral of order j. In the absence of barriers Eq. (1) returns immediately

$$K_s = -\frac{4\hbar N_D F_{-1/2}(\eta_F)}{3m^* \pi e^{\eta_F}}(k_B T)^{s-2}\int_0^\infty x^s \partial_E f(E, E_F)\,\mathrm{d}x \quad (8)$$

Note that Eq. (8) depends on the material properties upon N_D and m^* only. Equations (2) and (8) may be used to estimate η_F in real systems based upon their electrical conductivity, and therefore the PF may be obtained from Eq. (4) when no energy filtering occurs. Figure 1 displays the estimated PF in the case of *n*-type silicon.

In the presence of a barrier, instead, since in the parabolic-band approximation $r = 1/2$ and $p = -1/2$ for scattering due to either highly screened ionized impurities or acoustic phonons, Eq. (5) reads

$$K_s(1, x_b, \eta_F) = -\frac{4g_0\tau_0}{3m^*}(k_B T)^s\int_{x_b}^\infty x^s \partial_E f(E, E_F)\,\mathrm{d}x \quad (9)$$

Figure 2 shows the PF versus the potential barrier height E_b and the Fermi energy E_F normalized to the unfiltered case. The plot clearly shows an increase of the power factor with the introduction of a potential barrier. However, no increase larger than a factor 10 is predicted to occur. An even less remarkable improvement may be found in non-degenerate semiconductors.
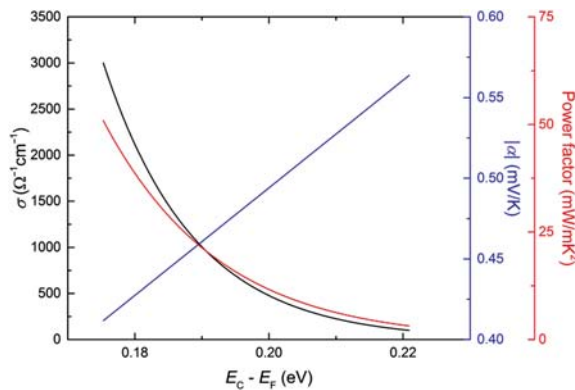

Figure 1. Electrical conductivity, Seebeck coefficient, and thermoelectric power factor of *n*-type silicon as a function of the Fermi energy (measured from the bottom of the conduction band).
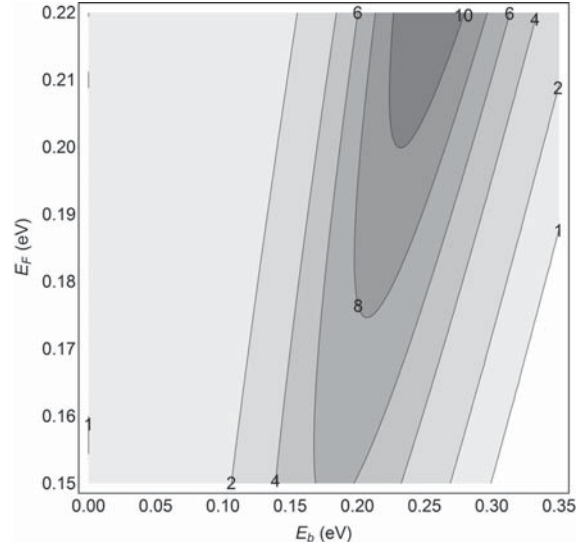

Figure 2. Thermoelectric power factor normalized to the unfiltered case as a function of the potential barrier height E_b and of its Fermi energy E_F.

2.3. Energy Filtering in Nanocomposites

This simple analysis considers x_b and η_F as two independent parameters. This is not the case in a homogeneous semiconductor, i.e., in the absence of impurities that may control the barrier height. Thus, this result does not contrast Heiliger's model[15] as long as the barrier height is set by heteroatoms segregating or anyway decorating the grain boundary. Additionally, this analysis relies upon the relaxation-time approximation, namely it is self-consistent as long as transport is diffusive. A fully quantum-mechanical analysis *not* using the relaxation-time approximation was proposed by Kim and Lundstrom.[22] Although limited to 1D systems, it is worth be compared to the current results to comment on the role played by the mean free path in energy filtering.

As mentioned, a critical analysis of relaxation phenomena requires distinguishing between two characteristic lengths, namely the momentum relaxation length λ_p and the energy relaxation length λ_E. Kim and Lundstrom showed[22] that in homogeneous semiconductors the largest improvement of PF is achieved when the barrier spacing d is intermediate between λ_E and λ_p, namely $\lambda_p < d < \lambda_E$. This is rather intuitive since for $d > \lambda_p$ no additional degradation affects σ (as transport is already diffusive) while $d < \lambda_E$ ensures that carrier energy does not relax within the interbarrier region, a phenomenon that would obviously cancel the PF enhancement. This theoretical conclusion is also in excellent agreement with experimental findings in silicon.[7] Should instead d be smaller than λ_p, apart from the inappropriateness of a relaxation-time approach to the problem, carriers would have no way to interact with the lattice itself over a distance d. Stated differently, barriers would be mostly ineffective to modify

electronic transport. This was quite well shown in the 1D case (nanowires), although no quantitative data are available in 3D systems.

This point is quite relevant when moving from single-phase to two-phase systems wherein, e.g., one phase is either a nanoprecipitate or a nanoinclusion. This is clearly the case of many nanocomposites. Two interbarrier distances describe these systems, one of which (d_1) is close to the grain size of the embedding phase while the other (d_2) is comparable to the nanophase size. Manifestly enough, $d_2 \ll d_1$. Correspondingly, two sets of relaxation lengths must be defined, one for each phase. The issue arises of how energy filtering eventually occurs when $\lambda_{p1} < d_1 < \lambda_{E1}$ while either $d_2 < \lambda_{p2}$ or $d_2 \approx \lambda_{p2}$ (with $\lambda_{p2} < \lambda_{E2}$). It is immediate to conclude that if no scattering occurs at the interface between the two phases ($d_2 < \lambda_{p2}$) no energy filtering may occur, so that the presence of the nanophase has no impact on the electronic transport (although it will affect the temperature distribution within the system—*vide infra*). Should instead carrier be scattered at the interface, a possible way to analyze the problem is to consider transport in each phase separately, namely dealing with the nanocomposite as a network of resistances pertaining to each phase. This second approach may be developed in a pseudo-1D model.[19, 23] Heterojunctions set the barrier at the interface between the two phases but, apart from the due corrections concerning the barrier height, the model inherits the results obtained in the one-phase system as long as single-phase conductivity and Seebeck coefficient are concerned. Within the pseudo-1D approximation one gets that the electrical conductivity σ of the composite is

$$\frac{\sigma}{\sigma_1} = \frac{d_{21}+1}{d_{21}/\sigma_{21}+1} \tag{10}$$

where $\sigma_{21} \equiv \sigma_2/\sigma_1$ (while σ_1 and σ_2 are the electric conductivities of the embedding and embedded phase, resp.)

and $d_{21} \equiv d_2/d_1$. A likely equation may be written for the thermal conductivity:

$$\frac{\kappa}{\kappa_1} = \frac{d_{21}+1}{d_{21}/\kappa_{21}+1} \tag{11}$$

where $\kappa_{21} \equiv \kappa_2/\kappa_1$ while κ_1 and κ_2 are the thermal conductivities of the embedding and embedded phase, resp.. As expected, both the thermal and the electrical conductivity are enhanced if $\sigma_2 > \sigma_1 (\kappa_2 > \kappa_1)$ and increase with d_2/d_1. Less obvious is the trend for α, that needs to be computed considering the actual distribution of temperatures originating from the different thermal conductivities of the two phases. Partitioning the applied ΔT over the two phases one easily computes that

$$\frac{\alpha}{\alpha_1} = \frac{\alpha_{21}d_{21}/\kappa_{21}+1}{d_{21}/\kappa_{21}+1} \tag{12}$$

where $\alpha_{21} \equiv \alpha_2/\alpha_1$ and α_1 and α_2 are the Seebeck coefficients of the embedding and embedded phase. Thus the nanocomposite PF and Z read

$$\frac{\text{PF}}{\text{PF}_1} = \frac{(d_{21}+1)(\alpha_{21}d_{21}/\kappa_{21}+1)^2}{(d_{21}/\kappa_{21}+1)^2(d_{21}/\sigma_{21}+1)} \tag{13}$$

and

$$\frac{Z}{Z_1} = \frac{(\alpha_{21}d_{21}/\kappa_{21}+1)^2}{(d_{21}/\kappa_{21}+1)(d_{21}/\sigma_{21}+1)} \tag{14}$$

where PF_1 and $Z_1 T$ are the power factor and the figure of merit of the embedding phase. Before analyzing the power factor and the figure of merit it may be worth noting that both the transport coefficients, the PF and Z in Eqs. (10)–(14) are *generic* quantities, i.e., they may refer to either filtering-enhanced or standard phases. Thus, two cases may be considered, namely that (a) the two phases
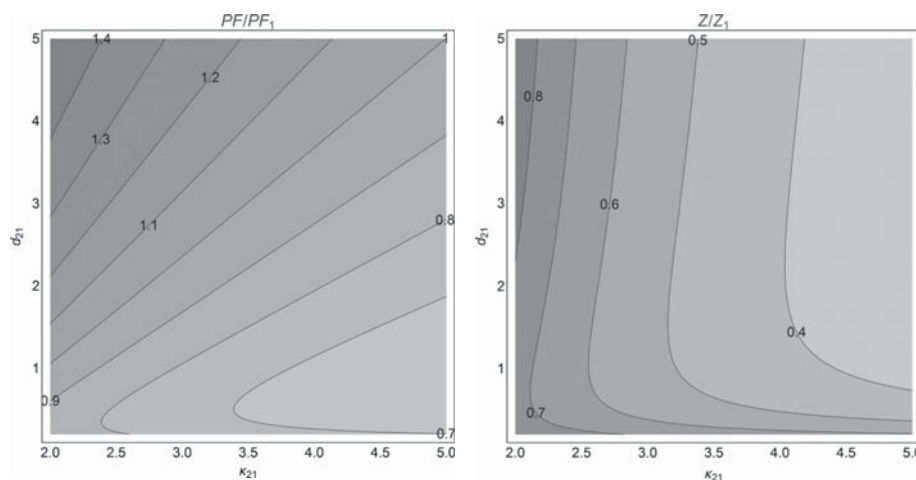

Figure 3. Normalized thermoelectric power factor (left) and figure of merit (right) of a pseudo-1D nanocomposite as a function of the ratio of the thermal conductivity in the two phases κ_{21}. Normalization was carried out with respect to the embedding phase while computation took $\text{PF}_2/\text{PF}_1 = 2$ and $\sigma_{21} = 0.2$.

contribute their unfiltered transport coefficients or that (b) the performance of the embedded phase is enhanced by energy filtering.

Figure 3 displays the enhancement of the power factor and of the figure of merit in case (a), namely the worst case. An enhancement of the power factor is observed for low κ_{21} and high d_{21}. While the growth of the PF with d_2/d_1 is trivial, as the embedded phase has by hypothesis a larger PF, the former dependency is possibly less obvious, and arises from the temperature dropping preferentially over the phase with the largest α. This remarkably implies that an enhancement of the composite figure of merit may result even in the absence of any energy filtering. The effective Seebeck coefficient actually depends not only on the Seebeck coefficients of the two phases but also of their thermal conductivity. Note however that in no case $Z > \max(Z_1, Z_2)$, as prescribed by the Bergman-Lévy theorem[24] in the absence of interfacial contributions to the transport processes.

3. DISCUSSION AND CONCLUSIONS

The occurrence of a simultaneous increase of the Seebeck coefficient and of the electrical conductivity is often taken as a landmark of energy filtering. This is justified by the fact that standard theory predicts that the two transport parameters should show the opposite dependency upon carrier density, as α should decrease when the carrier density increases while σ should have the opposite response. Invoking energy filtering may not be either appropriate or necessary, however. It has been remarked that in nanocomposites when barrier spacing disable any thermalisation mechanism (i.e., when charge transport is ballistic within the nanophase), no energy filtering may occur. Furthermore, the occurrence of energy filtering should be also checked toward ZT enhancement, as PF improvements may be due also to much simpler phenomena. It has been actually shown that also a simple partitioning of the applied temperature gradient over phases with different thermal conductivities might both cause an apparent improvement of the power factor (although not of the figure of merit).

In addition, a wealth of other physical effects, including resonant scattering,[25] modulation doping,[26, 27] and strain,[28, 29] might be responsible for a concurrent growth of α and σ. Thus, a more stringent and quantitative validation of the occurrence of energy filtering should be recommended before claiming energy filtering as the sole cause of improved thermoelectric performances in nanocomposites.

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