Concept of the Effective Mass and Minimal Thermal Conductivity of Superlattices

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Abstract

The periodic potential and its symmetry determine the energy band structure and as a consequence the effective masses of semiconductors. Superlattices do have a lower symmetry than the materials they are made of and they do have an additional long-range periodicity. Therefore the effective masses of superlattices should be a propertie of the superlattices itself and different of the one of its constituents. An increase of the Seebeck coefficient in the cross-plane direction, i.e. in the direction of growth of the superlattice, due to the filtering of electrons having energy below the Fermi level is expectable and an increase of the figure of merit may be attainable. In this article, the effective mass of an electron in a one dimensional rectangular periodic potential is derived in the tight-binding limit. The effective mass is found to be related to the energy band width calculated with the Kronig-Penney Model and the periodicity of the superlattice. The dependence of the figure of merit Z on the effective masse for a single conduction band and one type of charge carrier is discussed for bulk materials. The discussion is also done with the figure of merit derived by Dresselhaus for electrons in stacked quantum wells. Finally, the concept of minimal thermal conductivity of solid is reviewed and a method is proposed to compute the thermal conductivity of superlattices. The method of calculation proposed for the electronic and thermal properties suggest the possibility to derive a figure of merit which is much more related to the structure of the superlattices (periodicity, height of the energy barrier, interatomic distance and scattering mechanisms) and less related to the bulk material properties of the constituents.

Introduction

Fourteen years ago, Hicks and Dresselhaus did trigger a renewal of activity in the thermoelectric research area by proposing, in a very understandable way that quantum wells could have much higher figure of merit than the bulk materials [1]. The reason for this predicted increase was the higher dissymmetry in the electronic density of state at the optimal Fermi level achievable with low dimensional structures. This higher dissymmetry induces a more efficient filtering of the cold electron below the Fermi level. Just few years later, Venkatasubramanian did report a figure of merit of 2.4 in the cross-plane direction on Bi_2Te_3/Sb_2Te_3 superlattices [2], supporting the prediction made. Nevertheless, beside the surprisingly very good mobility [3], the improvement was much more the result of a reduction of the thermal conductivity [4], for which the value was slightly below the minimum thermal conductivity of solid calculated with the model of Cahill [5].

Nevertheless, the analytical model of Hicks and Dresselhaus is only valid for the calculation of the transport properties in the in-plane direction of a superlattice, i.e. in directions that are parallel with the plane of the quantum-well. This is because the charge carriers are restricted to move in this plane. Furthermore, the effective m^* mass that enters in the calculation of the density of state[1] per unit of volume of the 2D electron gas $g(E)$ is taken equal to that of the bulk material which is not valid since the unit cells of the superlattice is not the same that the one of the well [6]:

$$g(E) = \frac{m^*}{\pi \hbar^2 d} \sum_N \Theta(E - E_N) \qquad \text{(Eq. 1)}$$

where $\Theta(x)$ is the unit step function equal to 1 at x=1 and 0 at x<0, E_N the subband edge energies and d the thickness of the well (the thickness of the barrier is assumed to be zero but the height is infinite).

The specificity in the scattering mechanisms of electrons and holes in superlattices are likely to play an important role in the material of Ventakabrasubramanian but are not taken into account in the model of Hicks and Dresselhaus, the relaxation time being taken equal to a constant.

Therefore the model is insufficient to explain the experimental results. The correct method for calculating the density of states and the effective mass in the cross-plane direction is to use ab-initio calculation, i.e. to define a unit cells for the superlattice and to use algorithm like the APW, KKR or DFR methods [7-8]. Such methods have been used to explain the relatively high mobility of the superlattice of Ventakabramanian. It has been calculated that the effective mass was similar in the in-plane and cross-plane direction [9] and that the effective mass could be tuned (reduced) to enhance the mobility [10]. The figure of merit increases indeed with the ratio of the mobility (μ) to the lattice thermal conductivity (λ_{ph}) through the so-called quality factor [12, 13]. However, how the figure of merit change with a variation of the effective mass is not trivial. The mobility is of course an inverse function of the effective mass, but the density of states increase linearly with the effective mass in a 2D electron gas and even more quickly for a 3D electron gas ($\sim m^{*3/2}$). In fact, if the calculation of quality factor is carried out with the same hypotheses than Hicks and Dresselhaus, the quality factor (one band model, parabolic approximation) for a stacked 2D electron gas is [13]:

$$B = \frac{1}{d} \frac{\tau_0}{\pi \hbar^2} (k_B T)^{2+r} \frac{k_B}{\lambda_{ph}} \qquad \text{(Eq. 2)}$$

The quality factor for a bulk material with the same hypotheses is:

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[1] Assuming that the effective mass in the well is the same that in the bulk counterpart bulk material, the density of states can be higher than in the bulk.

$$B = \frac{1}{6\pi^2} \left(\frac{2k_B T}{\hbar^2} \right)^{5/2} \tau_0 m^{*1/2} \hbar^2 k_B \frac{1}{\lambda_{ph}} \qquad \text{(Eq. 3)}$$

where the relaxation time for the charge carrier has been written as a simple power law:

$$\tau = \tau_0 \varepsilon^r \qquad \text{(Eq. 4)}$$

r is called the scattering parameter.

Surprisingly, the quality factor for a stacked 2D electron gas is not strongly a function of the effective mass but a function of the scattering parameter whereas the quality factor of a bulk material is strongly a function of the effective mass but not of the scattering mechanism (the figure of merit is a function of the scattering mechanism). The quality factor of a real superlattice may be something between the one given by Eq.2 and Eq. 3 since the electrons may tunnel, or the interfaces of the superlattice may be imperfect.

Joffe found by optimizing $\sigma \alpha^2 / \lambda_{Ph}$ (σ =electrical conductivity, α = the Seebeck coefficient) that a low effective mass was better [11, p 173]. But by doing so, he did neglect the fact that low effective mass does also increase the electronic contribution of the charge carriers to the thermal conductivity. Mahan at the contrary did point out the fact that there is the combination $\mu m^{*3/2}$ in the quality factor of bulk materials, and that high effective mass may be in fact better [10, p 106].

The bias in favor of low effective masses is may be due to the low effective mass found in the material systems (Bi,Sb)$_2$(Te,Se)$_3$, which does follows the so called $10k_B T$ rule (T is the temperature where the figure of merit is maximal). The $10k_B T$ rule states that since λ_{ph} increase with band gap, i.e. with the decrease of the atomic weight, one wants materials with small gaps to keep λ_{ph} small. Nevertheless the gap must not to be too small because we want just one kind of charge carriers. As a consequence, the optimal band gap E_G of a thermoelectric materials is usually $\sim 10k_B T$. Since the effective mass decreases when the band gap is reduced [15, page 45],

$$m^* \sim \frac{m E_g}{E_G + 12 eV}$$

the small effective mass in (Bi,Sb)$_2$(Te,Se)$_3$ arises from the need for low thermal conductivity in thermoelectric materials and not a need for high mobility. After this introduction it is evident that the effective mass has to be maximized to increase the figure of merit when the electronic contribution to the thermal conductivity is not negligible. It is also concluded that an increase of the effective mass will produce a larger increase of the figure of merit when the lattice thermal conductivity is low. The objectives of this article was therefore to find a way to increase the effective mass and to figure out if the concept of minimal conductivity of solid could be apply to the superlattices.

In the next section, we will calculate the effective mass of an electron in a one dimensional rectangular periodic potential in the tight-binding limit. Even if the model is only valid for narrow energy band separated by wide band gap (certainly not the case of most thermoelectric materials), we would like to demonstrate that the effective masses can be tuned by varying the superlattice structure. In the section about the lower limit of the thermal conductivity of superlattice, we show that the Cahill's formula describing the minimum thermal conductivity of solids can be derived using the usual kinetic equation, just by taking a relaxation time for the phonons equal to π/ω. A simple explanation is given for this unusual relaxation time. Finally, some result of lattice dynamic studies are used to figure out if it is possible to get an even lower thermal conductivity with a superlattice than the one predicted by Cahill for bulk materials.

Effective mass in a periodic potential

Using the one dimensional tight-binding formula i.e. when the electrons are strongly bonded to the individual atoms or here when the electrons are almost trapped in a periodic potential (Figure 1), the energy dispersion can be approximated by [15, page 37]:

$$E_n(k) = E_n^c + (-1)^n \frac{\Delta_n}{2} \cos(kd) \qquad \text{(Eq. 5)}$$

which is valid when
1) The width of the energy bands Δ_n is narrow and separated by wide gaps,
2) The energy E of the electrons are lower than the height of the energy barrier V_0.

E_n^c denotes the center of the energy band, and d the period of the superlattice.

The band width can be approximated by [15, page 37]

$$\Delta_n = \frac{8(V_0 - E_n^c)}{\kappa(E_c^n) F'\left[\kappa(E_n^c)\right]} \exp(-\kappa(E_n^c)b) \qquad \text{(Eq. 6)}$$

where F' denotes the first derivative with respect to κ_z of the right-hand side of the following equation:

$$\cos(kd) = \cos(k_z a)\cosh(\kappa_z b)$$
$$+ \frac{\kappa_z^2 - k_z^2}{2\kappa_z k_z} \sin(k_z a) \sinh(\kappa_z b) \qquad \text{(Eq. 7)}$$

Where
$\hbar^2 k_z^2 = 2m E_{k_z}$ and $\hbar^2 \kappa_z^2 = 2m(V_0 - E_{k_z})$

Using Eq. 5, the energy near a minimum or maximum can be written as:

$$E_n(k) = E_n^c + (-1)^n \frac{\Delta_n}{2}\left(1 - \frac{k^2 d^2}{2} + ...\right) \qquad \text{(Eq. 8)}$$

Rearranging the terms and combining the factors in front of k^2 results in:

$$E_n(k) = E_n^0 + (-1)^{n+1} \frac{\hbar^2 k^2}{2m_n^*} + ... \qquad \text{(Eq. 9)}$$

Where $E_n^0 = E_n^c + (-1)^n \Delta_n / 2$ denotes the top (n even) or bottom (n odd) of the respective bands.

By identification between Eq.8 and Eq.9, the effective mass is found to be given by:

$$m_n^* = \frac{2\hbar^2}{\Delta_n d^2} \qquad \text{(Eq. 10)}$$

It can bee seen that the effective mass increases strongly when the superlattice period d decreases. Since Δ_n decreases exponentially with the barrier width b, it is also conclude that the effective mass will increase when the barrier width is decreased.
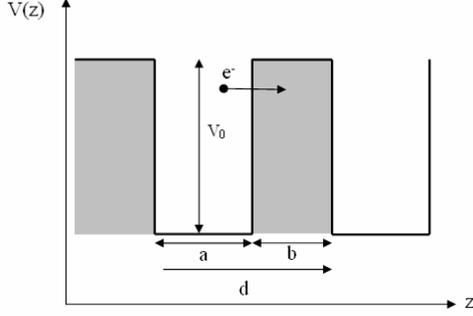

Figure 1: The rectangular periodic potential in the Kronig-Penney model.

Lower limit to the thermal conductivity of supelattices

Minimum in thermal conductivity of solid (Cahill's model)

We are demonstrating now that in the Cahill's model, a vibration mode of frequency f is assumed to exchange energy at a frequency $2f$ (like a clapper in a bell). Therefore it will be relaxed after a time $\tau = 1/(2f)$. The angular frequency ω being equal to $2\pi f$, the relaxation time will be:

$$\tau = \frac{\pi}{\omega} \qquad \text{(Eq. 11)}$$

Under the Debye approximation, it is assumed that dispersion relation is linear, so that:

$$\tau = \frac{\pi}{vk} \qquad \text{(Eq. 12)}$$

If we inject the heat capacity at constant volume [16]

$$C_v(k) = \frac{\hbar^2 v^2}{2\pi^2 k_B T^2} \frac{k^4 e^{\hbar vk/k_B T}}{\left(e^{\hbar vk/k_B T} - 1\right)^2} \qquad \text{(Eq. 13)}$$

into the algebraic expression of the lattice thermal conductivity [16]

$$\lambda_L = \frac{1}{3} \int \tau(k) v^2(k) C_v(k) dk \qquad \text{(Eq. 14)}$$

we obtain:

$$\lambda_L = \frac{1}{3} \int_0^{k_D} \frac{\hbar^2}{2\pi} \frac{v^3}{k_B T^2} \frac{k^3 e^{\hbar vk/k_B T}}{\left(e^{\hbar vk/k_B T} - 1\right)^2} dk \qquad \text{(Eq. 15)}$$

The integration is made from 0 to k_D, since we are working with the Debye approximation. k_D defines the Debye temperature which is given by:

$$\theta_D = \frac{\hbar v}{k_B} \left(6\pi^2 n\right)^{1/3} \qquad \text{(Eq. 16)}$$

Where n is the number of atoms per unit of volume and v the sound velocity.

After the change of variable $x = \hbar vk/k_B T$ in the Eq. 16, the equation becomes:

$$\lambda_L = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} v \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{x^3 e^x}{\left(e^x - 1\right)^2} dx \qquad \text{(Eq.17)}$$

This is the thermal conductivity for one acoustic mode either longitudinal or transverse. When the summation is done with two transversse and one longitudinal mode, the Eq. 17 is the same than the one derived by Cahill.

Minimum in the thermal conductivity of superlattice

It is well know that layered structures are efficient noise protection walls. The combination of different layers with different acoustic impedances and thicknesses reflects the sound waves so that the propagation of energy is impeded. In material science, the most computational time efficient method to get an insight into how well the energy propagate oneself in a superlattice is the calculation of the lattice dynamics [17]. The phonon density of level $g(\omega)$ and the dispersion relation $\omega(k)$ are calculable but no information about the relaxation time can be obtained with this method. Tamura and al found that the frequency dependent density of states weighted by the square of the group velocity in the cross-plane direction of a Si/Ge superlattice was strongly reduced [18]. With the same method, Yang and al. found that the phonon density of states in superlattices takes approximately the average values of the corresponding bulk materials. They confirm that the thermal energy propagation was strongly reduced in the cross-plane direction of the superlattice only [19]. An increase of the thermal conductivity was calculated when the layer thickness was decreased because of the tunneling of phonons. Nevertheless, the choice of the density of states weighted by the square of the group velocity as thermal energy propagation factor is open to criticism since it should be also weighted by the energy carried by the phonon, i.e. the heat capacity. Tamura et al did also calculate the ratio of thermal conductivity to the relaxation time, so that the heat capacity was taken into account. Similar results were obtained i.e the ratio of the thermal conductivity to the relaxation time was lower in superlatice than in bulk materials. Nevertheless when the ratio of the thermal conductivity to the relaxation time is calculated for the bulk material and the superlattice and when the results are compared, it is implicitly assumed that the relaxation time is independent of the angular frequency and that the relaxation time is the same for the bulk material and the superlattice. Therefore the method can not be used to calculate a lower limit to the thermal conductivity of the superlattice. The utilization of an angular frequency dependent relaxation time (like in the Cahill's model) along with the lattice dynamic calculations of the dispersion relations may be use in future to calculate the thermal conductivity of superlattices. Nevertheless, it is an open and interesting question whether the relaxation time used by Cahill and the dispersion relations calculated by lattice dynamics can be used in the same time. If it was the case, the thermal conductivity predicted for superlattices would be even lower than the minimal thermal conductivity of solid calculated by Cahill.

The parameter entering in the calculation of the relaxation times [15, 20] of the charge carriers (elastic constants, acoustic and optic deformation potentials …) and of the phonons (Grüneisen parameters, scattering cross-section,…) may be obtained with usual available computational tools in material science like molecular dynamic, provided that a suitable interatomic potential for a given material system is available [21].

Conclusions

To summarized, based on the Kronig-Penney Model and on results recently available in the literature, the effective mass can be tailored with a proper choice of the layer thicknesses of superlattices. A literature review about basic theories related to thermoelectric materials lead us to think that higher effective masses are better to get higher figure of merit, even if the mobility will be lowered. It is underlined that the bias in favor of low effective masses is likely to be due to the low effective masses found in the material system $(Bi,Sb)_2(Te,Se)_3$, which is a negative consequence of the fact that materials with heavy atoms does also have low thermal conductivity. The quality factors for bulk materials and a stacked 2D electron gas have been calculated with an energy dependent relaxation time of the charge carrier. The calculation suggests that the effect of the scattering mechanism on the figure of merit will be much more important in superlattices than in bulk materials. It is predicted that highly energy dependant scattering mechanisms are favorable in superlattice. Using the Kronig-Pennel Model of electrons in a periodic potential, we found that the effective mass in a superlattice may increase when the period is made shorter and the width of the barrier is decreased.

The axiom stating that the thermal conductivity is the lowest when all of the thermal excitations are scattered at a distance of one-half the wavelength, has be found undoubtedly equivalent with a relation time equal to π/ω.

References

1. L.D. Hicks, M.S. Dresselhaus, "Effect of quantum-well structures on the thermoelectric figure of merit", *Physical Review B*, Vol. 47, N° 19 (1993), pp. 12727-12731

2. R. Venkatasubramanian, E. Siivola, T. Colpitts, B. O'Quinn, "Thin-film thermoelectric devices with high room-temperature figures of merit", Nature, Vol. 143, N°11 (2001), pp. 597-602.

3. R. Venkatasubramanian, "Experimental evidence of high power factors and low thermal conductivity in Bi_2Te_3/Sb_2Te_3 superlattice thin-films, *Proc 15th International Conference on Thermoelectrics*, Pasadena, California March 1996, pp. 454-458.

4. R. Venkatasubramanian, "Lattice thermal conductivity reduction and phonon localization like behavior in superlattice structures", Physical Review B, Vol. 61, N°4 (2000), pp. 3091-3097.

5. D.G. Cahill, S.K. Watson, R.O. Pohl "Lower limit to the thermal conductivity of disordered crystals", Physical Review B, Vol. 46, N°10 (1992), pp. 6131-6140.

6. A. Shik, Quantum wells: Physics and Electronics of Two-Dimensional Systems, (World Scientific, London, 1997).

7. K. Ohno, K. Esfarjani, Y. Kawazoe, Computational Materials Science, from Ab Initio to Monte Carlo Methods, Springer series in Solid-Sate Sciences 129 (Springer Berlin Heidelberg, 1999).

8. C. Fiolhais, F. Nogueira, M. Marques, A Primer in density functional theory", Lectures notes in Physics, Springer, (Berlin Heildelberg, 2003).

9. H. Li, D. Bilc, S.D. Mahanti, "Theoretical study of electronic structures of Bi_2Te_3/Sb_2Te_3 superlattices", Thermoelectric materials 2003, *MRS-Proceedings, Research and Applications Symposium*, Vol. 793, pp. 339-444 (2004).

10. W. Guofeng, T. Cagin, "Investigation of effective mass of carriers in Bi2Te3/Sb2Te3 superlattices via electronic structure studies on its component crystals", Appl. Phys. Letters, Vol 89, N°15 (2006), 152101 pp. 1-3.

11. A.F. Joffe, L.S. Still'Bans "Physical problems of thermoelectricity", Report s on Progress in Physics N°22 (1959), pp. 167-203.

12. G.D. Mahan, "Good thermoelectrics", Solid State Physics, Vol. 51 (1998), pp. 81-157.

13. A. Jacquot "Engineering of thermoelectric materials and planar thermoelectric generators", dissertation of the Polytechnic Institute of Lorraine (France, 262p, (2003).

14. G.D. Mahan, "Figure of merit for thermoelectric", Journal of Applied Physics, Vol. 65, N°4 (1989), pp. 1578-1583.

15. H.T. Grahn, Introduction to semiconductor physics, World scientific, (Singapore, 1999).

16. R. Berman, "Heat conduction in non-metallic crystals", Scientific Progress, Oxford, Vol. 55 (1967), pp. 357-377.

17. M.T. Dove, Introduction to Lattice Dynamics, Cambridge Univesity Press, (New York, 1993).

18. S.I. Tamura, Y. Tanaka, H.J. Maris, "Phonon group velocity and thermal conduction in superlattices", Physical Review B, Vol. 60, N°4 (1999), pp. 2627-2630

19. B. Yang and G. Chen, Lattice Dynamics Study Of Anisotropic Heat Conduction In Superlattices, Microscale Thermophysical Engineering, Vol. 5 (2001), pp.107-116

20. J.M. Ziman, Electrons and Phonons – The theory of transport phenomena in solids, Oxford University Press (Oxford, 1960).

21. E.S. Landry, A.J. H. McGaughey, M.I. Hussein, "Molecular dynamics prediction of the thermal conductivity of Si/Ge superlattices", *Proc HT2007 ASME-JSME Thermal Engineering Summer Heat Transfer Conf*, Vancouver, British Columbia, July, 2007, HT2007-32152 pp.1-9.