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The effect of a multivalley energy band structure on the thermoelectric figure of merit

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Résumé. — Les coefficients de qualité thermoélectrique sans dimension de semiconducteurs à vallées multiples $(ZT)_{mv}$ ou à vallée unique $(ZT)_{sv}$ sont ici comparés. La diffusion des phonons acoustiques et celle des impuretés ionisées sont prises en considération. Bien qu'il soit avantageux pour les applications thermoélectriques d'utiliser un semiconducteur à vallées multiples, l'effet bénéfique est réduit par l'augmentation de la concentration des porteurs et la présence de diffusion inter-vallées. Lorsque la concentration des porteurs est optimale pour le coefficient de qualité thermoélectrique, le coefficient $(ZT)_{mv}/(ZT)_{sv}$ pour l'alliage silicium-germanium est réduit d'environ 40 %.

Abstract. — A comparison is drawn between the dimensionless thermoelectric figure of merit of a multivalleyed semiconductor $(ZT)_{mv}$ and one having a single valleyed structure $(ZT)_{sv}$. In the analysis both acoustic phonon scattering and ionized impurity scattering are considered. Although it is advantageous to employ a multivalleyed semiconductor in thermoelectric applications it is concluded that the beneficial effect of a multivalleyed structure is reduced with increase in carrier concentration and the presence of intervalley scattering. At a carrier concentration which optimizes the thermoelectric figure of merit, the ratio $(ZT)_{mv}/(ZT)_{sv}$ for silicon-germanium alloy is reduced by approximately 40 percent.

It has been generally accepted for some considerable time that a semiconductor which possesses a multivalley energy band structure should exhibit a higher value of the thermoelectric figure of merit Z than a similar material which has only a single valley. A comparison of the measured Z values for thermoelectric semiconductors supports this view. Multivalleyed semiconductors such as bismuth telluride, lead telluride and silicon-germanium alloys are the best materials over their temperature ranges of operation [1]. Previous analyses have shown that in the non-degenerate limit and neglecting intervalley scattering of the charge carriers, the figure of merit increases monotonically with the number of valleys N_v [2, 3]. In practice thermoelectric semiconductors are doped to relatively high carrier concentrations in order to optimize the materials thermoelectric properties. In the region of optimum doping, a multivalley energy band structure and the intervalley scattering may have a significant effect on the figure of merit compared to that in the non-degenerate limit.

In this note we report the results of our calculations into the effect of intervalley scattering on the figure of merit of a multivalleyed semiconductor, as a function of carrier concentration n

(expressed in terms of reduced Fermi energy ξ). Assuming conduction in a single band semiconductor (electron or hole) the dimensionless figure of merit for a multivalley semiconductor $(ZT)_{mv}$ (with N_v equivalent valleys) can be expressed as [1, 4]

$$(ZT)_{mv} = \frac{(\alpha'_e)^2 (\sigma'_e)_{mv}}{1 + (\sigma'_e \mathcal{L}_e)_{mv}} \quad (1)$$

where

$$\alpha'_e = \delta(\xi) - \xi \quad (1.1)$$

$$\delta(\xi) = \frac{(s + 5/2) F_{s+3/2}(\xi)}{(s + 3/2) F_{s+1/2}(\xi)} \quad (1.2)$$

$$\mathcal{L}(\xi) = \frac{(s + 7/2) F_{s+5/2}(\xi)}{(s + 3/2) F_{s+1/2}(\xi)} - \delta^2. \quad (1.3)$$

The reduced electrical conductivity σ'_e is given by

$$\sigma'_e = \beta \frac{F_{s+1/2}(\xi)}{(s + 1/2)!} \quad (2)$$

where

$$\beta = \frac{2(2\pi k_B)^{3/2} k_B^2 A'}{eh^3} \quad (2.1)$$

$$A' = T^{5/2} m^{*3/2} \mu / \lambda_L. \quad (2.2)$$

The various symbols have the same meaning as in reference [1].

Assuming that the reduced Seebeck coefficient α'_e is independent of the number of valleys and that the effect of intervalley scattering manifests itself primarily through the carrier mobility and electrical conductivity, the effect of a multivalley energy band structure on ZT can conveniently be discussed in terms of the ratio [5]

$$\frac{(ZT)_{mv}}{(ZT)_{sv}} = \frac{(\sigma'_e)_{mv} \{1 + (\sigma'_e \mathcal{L}_e)_{sv}\}}{(\sigma'_e)_{sv} \{1 + (\sigma'_e \mathcal{L}_e)_{mv}\}}. \quad (3)$$

In the non-degenerate limit, $-\xi \gg 1$ and in the absence of intervalley scattering

$$\frac{(ZT)_{mv}}{(ZT)_{sv}} = N_v. \quad (3.1)$$

The ratio $(ZT)_{mv}/(ZT)_{sv}$ can be evaluated as a function of the reduced Fermi energy or the carrier concentration, with ξ and n related by :

$$n = 4\pi \left(\frac{2k_B}{\hbar^2} \right)^{3/2} N_v m_d^{*3/2} T^{3/2} F_{1/2}(\xi).$$

Here m_d^* corresponds to the effective mass for a single valley i.e. $(m_1^* m_2^* m_3^*)^{1/3}$ where m_1 , m_2 and m_3 refer to the components of the effective mass tensor along the principal directions.

The model formulated is a general one and equation (3) can be solved by numerical integration for different scattering mechanisms. Silicon-germanium alloys are of particular interest to us and the various parameters employed in the calculations are appropriate to $\text{Si}_{70}\text{Ge}_{30}$. The important carrier scattering mechanisms operating in these alloys at room temperature are acoustic phonon scattering and ionized impurity scattering with associated scattering parameters $s = -1/2$ and $3/2$ respectively.

The material parameters A' are given by :

$$A'_{\text{acoustic}} = \frac{(8\pi)^{1/2} e \hbar^4}{3 k^{3/2}} \frac{C_{11}}{\varepsilon_1^2 \lambda_L} \frac{T}{m_c^*} \frac{N_v}{m_c^*}$$

and

$$A'_{\text{impurity}} = \frac{2^{7/2} k^{3/2} \chi^2 m_d^{*2} T^4 (N_v/m_c^*)}{\pi^{3/2} e^3 N_1 \lambda_L \ln \left[1 + \left(\frac{3 \chi k T}{e^2 N_1^{1/3}} \right)^2 \right]}.$$

Where ε_1 is the acoustic deformation potential, C_{11} is the longitudinal elastic constant, χ is the dielectric constant and N_1 is the concentration of ionized impurities (when each of the ionized impurities contribute one free electron, $N_1 = n$).

Results.

The ratio $(ZT)_{mv}/(ZT)_{sv}$ for $\text{Si}_{70}\text{Ge}_{30}$ alloy at 300 K is displayed in figure 1 as a function of carrier concentration. Both acoustic phonon scattering and ionized impurity scattering are considered, but without the inclusion of intervalley scattering. Both mechanisms lead to a value of $N_v = 6$ in the non-degenerate limit and this value decreases with an increase in carrier concentration. The pattern of the decrease in the ratio $(ZT)_{mv}/(ZT)_{sv}$ with carrier concentration is different for each mechanism. In the acoustic scattering case the decrease in this ratio occurs over the range of carrier concentration from 10^{24} to 10^{26} m^{-3} , while for ionized impurity scattering the ratio remains almost constant at $N_v = 6$ up to a carrier concentration of 10^{25} m^{-3} and then decreases rapidly with increase in carrier concentration.

The exclusion of intervalley scattering may not be justified, particularly at high temperatures, and intervalley scattering is likely to have a significant effect on the thermoelectric figure of merit. Acoustic intervalley scattering is included in our calculations by following a method due to Herring [6]. An expression is obtained for the temperature dependence of the carrier mobility

Fig. 1. — The ratio $(ZT)_{mv}/(ZT)_{sv}$ as a function of carrier concentration for $\text{Si}_{70}\text{Ge}_{30}$ alloy at 300 K. Curve 1 : acoustic phonon scattering. Curve 2 : ionized impurity scattering.

Fig. 2. — The ratio $(ZT)_{mv}/(ZT)_{sv}$ as a function of carrier concentration for $\text{Si}_{70}\text{Ge}_{30}$ alloy at 300 K. Acoustic phonon scattering. Curve 1 : no intervalley scattering, $W_2/W_1 = 0$. Curve 2 : intervalley scattering included, $W_2/W_1 = 2.0$.

as a function of the ratio W_2/W_1 , where W_2 and W_1 are measures of the strength of the carrier coupling to intervalley and intravalley acoustic modes respectively. The ratio W_2/W_1 is adjusted to give realistic values of the carrier mobility and the figure of merit. In figure 2 is displayed $(ZT)_{mv}/(ZT)_{sv}$ as a function of carrier concentration, assuming acoustic phonon scattering with (a) intravalley scattering, (b) intra and intervalley scattering.

The inclusion of intervalley scattering does not appreciably affect the ratio $(ZT)_{mv}/(ZT)_{sv}$ at low carrier concentrations. However, as is evident from the figure, its effect increases with increase in carrier concentration. It is concluded that intervalley scattering significantly reduces the beneficial effect of a multivalley energy band structure. At optimum doping level in silicon-germanium alloys ($n \sim 10^{25} \text{ m}^{-3}$) intervalley scattering reduces the ratio $(ZT)_{mv}/(ZT)_{sv}$ by approximately 40 %.

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