Theoretical analysis of thermoelectric power of nanocrystalline ReSi$_2$ thin film

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Abstract. The formulation is developed for the predictive modeling of thermoelectric power ($S$) of nano-crystalline ReSi$_2$. We have evaluated the phonon thermoelectric power by incorporating the scattering of phonons with impurities, grain boundaries, charge careers and phonons. It is noticed that at low temperatures ($T < 400$ K), $S$ increases and show power temperature dependence because of the larger mean free path of phonon, $S$ shows a broad peak at about 550 K, which is artefact of the competition among umklapp scattering and grain boundaries scattering. Further, by increasing temperature $S$ decreases with change in slope. The anomalies are well accounted in terms of interaction among the phonons-impurity, phonon grain boundaries and the umklapp scattering. Under certain conditions grain boundary scattering is expected to be more effective on heat carrying phonons than on Umklapp scattering, causing an increased thermoelectric power. Numerical analysis of thermoelectric power from the present model shows similar results as those revealed from experiments.

1. Introduction

The Nanocrystalline composites (NC) retained some attentions due to their applications in silicon microelectronics technology. Despite the great interest for applications of these materials, a lot of their fundamental questions still remain unanswered. Electronic transport properties of NC conductors are strongly affected by the interaction of conduction electrons with the interfaces. In NC metals the interfaces represent an additional scattering channel for the conduction electrons, resulting in an enhanced resistivity of the NC metals, and some effects on thermopower [1–3]. The simple $T^{-3/2}$ dependence of the mobility is generally found in semiconductors and considering the electron-phonon scattering mechanism can derive it [4]. An obvious attractive feature of NC composite thermoelectrics is that their thermal conductivity is drastically reduced in comparison with conventional polycrystalline counterparts [5]. Burkov et al. have found that the transport properties of Re-Si thin films consisting of amorphous and NC phases do not follow the Effective Medium Approximation predictions. On the contrary, $S(x)$ reveal nonmonotonic variation. This implies that the interfaces between the amorphous and NC phases strongly influence the transport properties of the films [6].

Experimental data [7] for thermoelectric power $S$ ($T$) of ReSi$_2$ shows anomalous temperature dependent behaviour. The thermoelectric power is a powerful probe to understand not only the electronic structure but also shed light on the electron-phonon interaction. In present investigation we plan to seek the role of scattering of phonon with defects, grain boundaries, phonon and electrons for
phonon drag thermoelectric power ($S_{\text{ph}^{\text{drag}}}$) as well the carrier diffusion contribution ($S_{\text{c}^{\text{diff}}}$). This improves our understanding of the interplay of scattering processes between the heat carriers themselves and between the carriers and the impurities for the explanation of the reported behaviour of the thermoelectric power $S(T)$.

2. The model

Let us begin by constructing a model Hamiltonian [8]

$$
H = \sum_p \varepsilon_p a_p^+ a_p + \sum_q \omega_q b_q^+ b_q + \sum_{p_1, p_2} \phi(p_1, p_2) a_{p_1}^+ a_{p_2} + D_p \sum_q \frac{\hbar}{2 \rho \omega_q} a_{p+q}^+ a_p (b_p + b_q^+) \\
+ \frac{R}{2n} \sum_{q_1, q_2} \epsilon(q_1 + q_2) R \left[ \frac{\hbar \omega_{q_1} \hbar \omega_{q_2}}{4} \right]^{1/2} (b_{q_1} - b_{q_1}^+) (b_{q_2} - b_{q_2}^+) + H_{p-p}.
$$

(1)

The initial two terms are carrier (electron), and phonon excitation, the third and fourth terms represent carrier-impurity and carrier-phonon interactions, respectively. The fifth term is phonon-impurity interaction and last term stands for the phonon-phonon interaction. The symbols appeared in equation (1) are: $\varepsilon_p$ the carrier free energy, $a$ ($a^+$) and $b$ ($b^+$) are the creation (annihilation) operators for electron and phonon, $\phi$ is coupling parameter of electron and impurity potential, $D_p$ is deformation-potential constant, $\rho$ is ionic mass density, $\omega_q$ is acoustic phonon frequency of a wave vector $q$, $R$ is relative ionic-mass difference ($[(M''-M)/M'']$), $M$ ($M''$) symbolizes for Si$_2$ (Re), number of cells is $n$ and $R_i$ stands for the position of defects due to substitutions.

To estimate the phonon drag thermoelectric power, we shall use the Kubo formula [9] following model Hamiltonian. It has contributions from both the phonons and the carriers. In the continuum approximation the lattice part follows [10]

$$
S_{\text{ph}^{\text{drag}}}(T) = \frac{k_B}{\Theta_D} \left[ \frac{T}{\Theta_D} \right]^3 \int \frac{d\omega}{\omega^5} A(\omega) (\beta\omega)^4 e^{\beta\omega} (e^{\beta\omega-1})^2.
$$

(2)

$k_B$ is being the Boltzmann constant, $e$ is the charge of carriers, $\omega_D$ is the Debye frequency and $\beta=\hbar/k_BT$.

The relaxation time is inhibited in $A(\omega)$ and is proportional to the imaginary part of the self-energy $\Sigma$. The relaxation times ratio can be calculated to the lowest order of the various interactions in the weak interaction case. The phonon drag thermoelectric power relaxation times ratio $A(\omega)$ follows

$$
A(\omega) = [1/\tau_{\text{ph-d}} + 1/\tau_{\text{ph-gb}} + 1/\tau_{\text{ph-c}}] [1/\tau_{\text{ph-d}} + 1/\tau_{\text{ph-gb}} + 1/\tau_{\text{ph-c}}]
$$

(3)

The relaxation times are expressed as

$$
1/\tau(\omega) = 2\left| \text{Im} P(\omega) \right|
$$

(4)

The various relaxation times are defined in terms of transport coefficients as

$$
\tau_{\text{ph-d}}^{-1}(\omega) = D_{\text{ph-d}} \left[ k_B^3/\omega^4 \hbar^3 \right],
$$

(5)

$$
\tau_{\text{ph-gb}}^{-1}(\omega) = D_{\text{ph-gb}} v_s/L,
$$

(6)

$$
\tau_{\text{ph-c}}^{-1}(\omega) = D_{\text{ph-c}} \left[ T \omega h / k_B \right]^3
$$

(7)

and

$$
\tau_{\text{ph-d}}^{-1}(\omega) = D_{\text{ph-d}} n_F(\Delta),
$$

(8)

$v_s$ being the velocity of sound, $L$ is the crystal dimension, $n_F$ is the Fermi-Dirac distribution function and $\Delta$ is the energy gap parameter. The notation $\tau_{\text{ph-d}}$, $\tau_{\text{ph-gb}}$, $\tau_{\text{ph-c}}$ and $\tau_{\text{ph-c}}$ are the phonon scattering relaxation time due to substitutional defects, grain boundaries, phonon and phonon-carrier interactions respectively.

The transport coefficients appearing in equations (5 – 8) are defined as
\[ D_{\text{phd}} = \frac{3n_iR^2}{4\theta_D^3} \quad \text{and} \quad D_{\text{phe}} = \frac{9\pi}{4} \left[ \frac{m}{3M} \right]^{1/2} \frac{D_p^2}{\varepsilon_F^2} \]  

(9)

with \( n_i \) is the density of impurities or point defects, \( R \) is the relative ionic-mass difference \( \theta_0 \) the Debye temperature, \( m \) the carrier mass, \( M \) the ionic mass and \( \varepsilon_F \) the Fermi energy.

We shall now proceed to include the effect of electron as carrier diffusion contribution for thermoelectric power contribution employing the well-known Mott formula. The carrier diffusion thermoelectric power [10] is

\[ S_{\text{diff}}(T) = -\frac{\pi^2 k_B^2 T}{3|\varepsilon|} \left[ \frac{\partial \ln \sigma(\varepsilon)}{\partial \varepsilon} \right]_{\varepsilon=\varepsilon_F} \]  

(10)

with \( \sigma(\varepsilon) = ne^2\tau(\varepsilon)/m \) is the energy dependence of electrical conductivity in the relaxation time approximation. Here, \( n \) and \( m \) are the density and the mass of carriers respectively and \( \tau \) the relaxation time. Moreover this expression is true if also the free electron approximation is assumed and not the relaxation time approximation alone. For the sake of simplicity, it is sufficient to neglect the energy dependence in \( \tau(\varepsilon) \) taking \( \tau(\varepsilon) = \tau(\varepsilon_F) \), the equation (10) becomes

\[ S_{\text{diff}}(T) = -\frac{\pi^2 k_B^2 T}{3|\varepsilon|\varepsilon_F} \]  

(11)

Keeping in mind that \( \tau = \ell/v_F \), the method point to the scattering of carriers by impurities is dominant for constant relaxation times.

3. Results and Discussion

For the actual calculation of thermoelectric power of the Nanocrystalline composites ReSi\(_2\) we make use of the transport parameters which characterize the strengths of the phonon-defects, phonon-grain boundary, phonon-phonon (umklapp) and phonon-carrier scattering process as \( D_{\text{phd}} = 2.1 \times 10^{-5} \text{ K}^{-3} \), \( D_{\text{phph}} = 3.31 \times 10^{-3} \), \( D_{\text{phc}} = 0.6 \times 10^{-2} \text{ K}^{-6} \text{ sec}^{-1} \) and \( D_{\text{phe}} = 1.8 \) respectively. These are material dependent fitting parameters for phonon drag thermoelectric power in the present model.

We first qualitatively discuss the phonon drag thermoelectric power in the presence of various scattering mechanisms. The main finding of phonon drag thermoelectric power \( S_{\text{ph drag}} \) is that at low temperatures \( T < 400 \text{ K} \), \( S \) increases and show power temperature dependence because of the larger mean free path of phonon, the quasi particle excitations condensed into the ground state and they cannot scatter phonons. \( S_{\text{ph drag}} \), thus, increases exponentially with temperature. Although \( S_{\text{ph drag}} \) experiences an exponential increase at low temperatures, the presence of the impurity, grain boundaries and the carriers scattering set a limit on its growth, as a consequence \( S_{\text{ph drag}}(T) \), change a slope at moderate temperature and develop a broad peak around 500 K and then decreases with further increase in temperature. This dependence of thermoelectric power is one of the interesting features of ReSi\(_2\). The change in slope at different temperature depends on the relative magnitudes of the phonon-defect, phonon grain boundary and phonon-phonon umklapp scattering processes. In Nanocrystalline thin films like ReSi\(_2\), due to the grain size of the order of nanometers, the grain boundaries scattering become more effective in most of the temperature range. However the phonon-phonon umklapp scattering become more effective at higher temperatures as a consequence the phonon mean free path decreases which demolish the thermopower at higher temperature (see figure 1).

Let us now estimate the carrier diffusion thermoelectric power \( S_{\text{diff}} \), which is given by the expressions (10 and 11), which is inversely proportional to Fermi energy \( \varepsilon_F \). The carrier-impurity contribution to the thermoelectric power \( S_{\text{diff}} \) is documented in figure 1 as functions of temperature. It is evident from the plot that \( S_{\text{diff}}(T) \) increases linearly with increasing temperature. Finally both contributions are added together and plotted with experimental data [1] in the same figure. Numerical analysis of thermoelectric power from the present model shows similar results as those revealed from
experiments. $S(T)$ behavior depends on the competition among the various scattering mechanisms for the heat carriers and balances between the electron and phonon competition.

Figure 1. Variation of thermoelectric power with temperature. Experimental data is taken from Burkov et al. 1996 [7].

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