Colossal Seebeck coefficient of thermoelectric material calculated by space charge effect with phonon drag background

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We present colossal Seebeck coefficient (*S*) and large thermal electron motivate force (EMF) reproduced by space charge (SC) effect, introducing multi-Debye lengths into grain boundaries (GBs) of thermoelectric (TE) materials with phonon drag (PD) effect. Recently colossal *S* was reported in several TE materials. In addition, the polarity reversal was also reproduced by transfer process with inner bias around SP generated from thermal EMF. Colossal *S* and EMF for TE material were reproduced by SC model as the functions of Debye length into GBs, reduced mass: m^*/m , and temperature.

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1. Introduction

Recently, colossal Seebeck coefficient (S) has reported in the experimental studies about several thermoelectric (TE) materials, and it can be estimated by space charge (SC), and phonon drag (PD) models. TE properties of various TE materials have been understood in view of Fermi integral (FI) method, narrow band model [1-3] and space charge (SC) model etc. [4,5] Nowadays, colossal S with SC model defined at low temperature is firstly proposed about *n*-type FeSb₂ (FS) [4,5], and/or PD effect. [6,7] In addition, reversal Cu₂Se (CS) [8], and *n*-type $SrTiO_3$ (STO) [1] are also paid attention for highly S. Figure 1 shows TE properties of FS at around 10K, CS, and STO at around ~400K. Highly S was reported in FS at 10K, as shown in Fig.1 (a) at low temperature (~10K), and polarization reversal is reported in CS room temperature (RT) with comparing STO, as shown in **Fig.1** (b).



Fig.1 TE properties of (a) n-type FeSb₂, (b) polarity reversal Cu₂Se and n-type SrTiO₃ versus temperature. The polarity reversal of Cu₂Se is considered caused by charge transfer process.

In this report, we report the result of reproducing colossal *S* with introducing multi-Debye length (q_D) inner GBs in TE material with PD effect background. [6,7]

2. PD, SC model and calculations

Thermoelectric (TE) properties were calculated for 2-1 phonon drag (PD) effect, 2-2 interface space charge (SC) around electrodes, and inner SC effect at each grain boundaries (GBs). The band SC models are shown in **Fig.2**. [4,5] In SC models, the carriers were defined as thermally diffused for an electrode accompanied with inner SC.

2-1 Phonon drag effect

Seebeck coefficient caused by phonon drag (PD) effect (S_{pd}) is represented as the functions of length (l_k, l_s) , as follows,

$$S_{pd} = C\beta v_a l_s / (\mu)T, \qquad (1)$$
$$l_k = \beta l_s, \qquad (2)$$

where *C*, β and μ are coefficients (0.17e+3~3.5e+3, ~0.9), and drift mobility (1e-3 m²/Vsec), respectively.

2-2 Interface, and inner space charge effect

In calculation, the interface SC were firstly calculated based on model I, then inner SC state was calculated based on model II.

The interface SC effect as for model I, was estimated as follows,

$$V = (3/2)^{4/3} (-j/A)^{2/3} (m^*/2e)^{1/3} x^{4/3} + SdT,$$
(3)

where carrier charging around electrode (1st term), and usual thermal EMF (2nd term ~0), as follows $V=V_{ele}+SdT\sim V_{ele}$, where $j=\sigma(T)E$, j/A, and, m^* relating with temperature dependence of mobility $\mu\sim(m^*/m_0)T^*$ $^{3/2}$, are current, current density: $10^{-6}\sim10^{-3}$ A/m², and $0.1m_0\sim2m_0$, respectively.

Thermal EMF by SC was also calculated by using Poisson's eq. $(d^2V(x)/dx^2 = \rho'\varepsilon)$, as for SC model II, as shown in **Fig.2(b)**. Thermal EMF and *S* were estimated, as follows,

$$V_{1}=|V(L)/V(0)|$$

$$=\Sigma(\mathcal{E}/q_{D})[q_{D}l(1+\exp(-q_{D}l))+2\exp(-q_{D}l)-2], \qquad (4)$$

 $S = -(V/dT) \{ f(q_{\rm D}l) \},$ (5)

where $f(q_D l)$ equals $1-(2/q_D L) \tanh(q_D l/2)$. N, \mathcal{E} , q_D , and L are carrier density, $eA/\varepsilon_0 \varepsilon_t q_D$ at each GBs, Debye length ($\lambda_D=1/q_D$) inner GB as temperature variation, and sample length, respectively. In calculation, q_D versus T with GBs and EMF versus length were estimated.

The single $\lambda_D = 1/q_D$ (represented as $q_D^2 = q^2 N_e / \epsilon k_B T$), and $q_D l$ (length: $l=100 \mu$ m) are estimated as 0.2 cm, and 50 mm orders, respectively.

In addition, the multi- q_D was set at grain boundaries (GBs) for series connection. [4,5]



Fig.2 Band SC models for *n*-type TE material, (a) interface SC with inner electric field (E_{in}) around electrode : model I, with (b) inner space charge (SC) with defect structure : model II, and Debye length versus (c) length as a function of *T*, and versus (d) *T* as a function of *N*.

3.Results and discussion

3-1 Polarity reversal

As shown in **Fig.2(a)**, inner thermal EMF carrier charging around electrode was simply calculated from current density due to inner electric field for *n*-type TE material as for SC model I, as follows, eq.(3). In calculation, EMF, and S versus length as the functions of current density, and m^*/m were estimated.



Fig.3 Polarity of thermal EMF versus (a) time (t, calculation: m^*/m_0 purple:2, green:1, blue:0.1), and (b) T of CS fitted by eq.(4) from SP model I (blue-line: exp.[8], red-line: calculation).

The polarity reversal of thermal EMF is caused with increasing electric field of SC than that of EMF, and effective length for electric field: x_1, x_2, S is considered in view of the process of increasing and decreasing

voltage as a function of m^*/m_0 .

The time dependence of thermal EMF as the functions of m^* , and τ . Inner bias is written as

 $V=E(eE/2m^*)(t/\tau)^2$. (6) From eq. (6): $m^*v^2/2=eE(eE/2m^*)(t/\tau)^2=eEx=eV=k_{\rm B}T$, where τ is life time. Polarity reversal is caused by carrier transfer of CS, and formation of SC.

3.2 SC model I

Figure 4(a) shows length dependence of thermal EMF and *n*-type *S* in TE material as a function of m^*/m calculated by using eq.(3). Following SC model I in Fig. **4(a)**, input to 1.0×10^{-3} A/m² (1.0×10^{-7} A/cm²), 1.0×10^{-6} A/m² (1.0×10^{-10} A/cm²), ε_i =10, m^*/m_0 =0.1, 1, 2, and dT=10K. The profile of thermal EMF in Fig.4(a) is similar with that of SP model I calculation in Fig.2(d). The inner electric field in SC region(s) is about $1.6 \times 10^{+3}$ V/m. From 0 m to 0.5×10^{-2} m, SC is charged with inner electric field (E_{in}).

3.3 SC model II with GBs

Figure 4(b) shows length dependence of EMF and *S* by using eq.(4). The voltage and *p*-type *S* profiles are calculated by eq.(4) using $q_{\rm D}$. $q_{\rm D}$ is set to 0.2 cm at GBs (grain size: 100 μ m), by modifying $q_{\rm D}=cN/(\epsilon k_{\rm B}T)^{1/2}$ with $N=10^{+18}\sim10^{+19}$ cm⁻³, and $\epsilon=10$.



Fig.4 Thermal EMF and *S* versus sample length profiles (a) calculated by using eq.(3) from model I: 1×10^{-3} A/m², and (b) calculated by using eq.(4) from model II by using averaged-*q*_D.

4.Conclusion

Thermoelectric properties (EMF, *S*) were calculated by interface and inner space charge (SC) models using multi-Debye length, as follows (1) carrier charging SC interface around electrode, and (2) SC in inner TE material. The carriers are thermally diffused for an electrode accompanied with inner SC, and thermal EMF from inner SC to carrier charging around interfaces with inner bias is effective for *S*, and it is the origin of large EMF and colossal *S*, although voltage polarity reverse was appeared by inner bias.

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