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Development of a Seebeck Coefficient Prediction Simulator Using Tight-Binding Quantum Chemical Molecular Dynamics

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1. Introduction

The search for high-performance thermoelectric materials is a subject of current intense research. The performance of thermoelectric materials or devices depends on the dimensionless figure of merit *ZT* of the materials which is given by $ZT=(S^2\sigma T/\kappa)$ where S, σ, T, and κ are the Seebeck coefficient, absolute temperature, electrical conductivity and total thermal conductivity, respectively [1]. The best materials available today for devices operating near room temperature are doped semiconductor alloys of antimony and bismuth telluride [2-5] which have a *ZT* equals to 1. However, for practical purposes, a suitable high-performance thermoelectric material should have a *ZT* of at least 4. Increasing *ZT* by a factor of 4 has remained a formidable challenge. Many approaches to increase the *ZT* of materials have been explored, for instance quantum-well structures [6], thin film and multilayer materials [7], crystals with complex electronic structures [8], and a class of compounds with a behavior similar to electron-crystal phonon glasses which have electrical properties of crystalline materials and the thermal properties of a glass [9]. To improve the rational design of high-performance thermoelectric materials, a fundamental understanding of the *ZT* as well as its theoretical prediction, especially the Seebeck coefficient, based on crystal and electronic structure are necessary.

Most of the existing theoretical studies for the thermoelectric properties use continuum models (e.g. effective mass approximation) because of their computational efficiency [10]. However, continuum models cannot take into account atomic level effects due to, for example, interface states in quantum-wire/well superlattices and surface states in quantum wire/wells. On the other hand, most of the *ab initio* models, which are atomistic by definition, do not scale well in terms of computational time as the number of involved atoms increases. A parameterized tight-binding model bridges the gap between the poorly scalable atomistic models and the scalable non-atomistic models. The tight-binding model is atomistic, yet computationally efficient due to the reduced number of basis orbitals and the flexible parameterization of the Hamiltonian.

In our previous work [11,12], we developed new prediction methods for the determination of both electrical and thermal conductivity. In this work, we have succeeded in the development of a Seebeck coefficient predictor based on tight-binding quantum chemical molecular dynamics method.

2. Computational Method

We have developed a new evaluation method for Seebeck coefficient based on a tight-binding quantum chemical molecular dynamics calculation using our original developed program "Colors". "Colors" is over 5000 times faster than the conventional first-principles molecular dynamics approach, because this program employs various parameters in order to accelerate the quantum chemical molecular dynamics calculations. In order to maintain the accuracy and the generalization of the tight-binding quantum chemical molecular dynamics approach, we developed a new methodology to determine all the parameters by fitting the results to first-principle calculation results. This methodology enables us to perform fast and accurate quantum chemical molecular dynamics simulations. This underscores the importance of the "Colors" systems in calculations for large-scale complex systems and thermoelectric materials as compared with other systems.

In the present work, the Seebeck coefficient is evaluated by using the following equation (1):

$$S=\frac{1}{eT}\frac{\frac{2}{m^*}\sum_{\varepsilon_k}\Delta\varepsilon\left[\frac{\beta\exp(\beta(\varepsilon-\mu))}{(1+\exp(\beta(\varepsilon-\mu)))^2}\right]\rho(\varepsilon_k)\varepsilon_k(\varepsilon_k-\mu)}{\frac{2}{m^*}\sum_{\varepsilon_k}\Delta\varepsilon\left[\frac{\beta\exp(\beta(\varepsilon-\mu))}{(1+\exp(\beta(\varepsilon-\mu)))^2}\right]\rho(\varepsilon_k)\varepsilon_k} \qquad (1),$$

where, ε_n is the energy level of each molecular orbital, $\rho(\varepsilon_n)$ is the electronic density of states, $\Delta\varepsilon$ is the ouput interval of the energy for the density of sates, e is the elementary charge, T is the absolute temperature, m^* is the effective mass, β is $1/k_BT$ (k_B is the Boltzmann constant), and μ is the Fermi level, respectively. The information for ε_n, $\rho(\varepsilon_n)$, and $\Delta\varepsilon$ are obtained from tight-binding quantum chemical molecular dynamics program "Colors".

On the other hand, to evaluate the Fermi level of the system, we also developed a new program. This new program can evaluate the Fermi level considering the balance of the number of thermal excited electrons and holes among the molecular orbitals that are calculated using tight- binding quantum chemical molecular dynamics for the system under investigation.

3. Results and Discussion

In order to demonstrate the effectiveness of our new methodology, we have applied it to the calculation of a Pt model frequently used as thermocouple in temperature measurement devices. The model contains 108 atoms in a periodic boundary condition cell of 11.7571 Å, 11.7597 Å, and 11.7542 Å of size. Preliminary relaxation calculation was performed at 273 K by classical molecular dynamics as described in a previous report [12]. The relaxed calculation model is shown in Fig. 1.

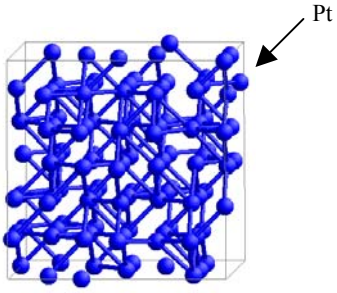

Fig. 1 Calculation model of Pt crystal

First of all, in computing the density of states consists using our tight-binding quantum chemical molecular dynamics program "Colors" through equation (1). The result is shown in Fig. 2. In this figure, the singly occupied molecular orbital is set to 0 eV. Figure 2 shows that the density of states is across the 0 eV. This result reflects the electronic properties of the metal, and shows that our original tight-binding quantum chemical method is able to reproduce the electronic features of metallic materials with fair accuracy.

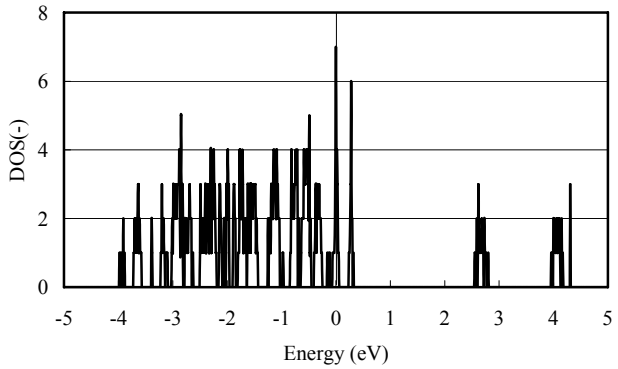

Fig. 2 Density of states of Pt crystal model by tight-binding quantum chemical molecular dynamics program "Colors"

To obtain the appropriate Fermi level, we counted the number of thermal excitation electrons and holes using the Fermi distribution function at an operating system temperature of 273 K. The appropriate Fermi level was that for which the number of electrons and holes are equal. Our newly developed program assumes, at first, that the energy of a Fermi level is the same for all singly occupied molecular orbitals. According to this assumption, the distribution of thermally excited electrons and holes for the molecular orbitals is estimated. If the number of electrons and holes is not the same, the program adopts the revised energy level as the new Fermi level. Applying this procedure recursively, the equality of the number of electrons and holes is obtained for a particular energy level.

Based on the above, the Seebeck coefficient is calculated by our new program. The result of this computation is shown in Table 1. The computational and experimental results show a fair agreement. This result has roots in the precise information of the electronic structure for the system. Although the comparison was made only on one crystal model and more examples are of cause needed to validate our new method, it should be emphasized here that our methodology is non-empirical and therefore might be applicable to wide range of large-scale complex systems.

Table 1 Calculated and experimental value of Seebeck coefficients

Seebeck coefficient (μV/K)	
Calculated	Experimental
-5.62	-4.45

4. Conclusions

We have succeeded in the development of Seebeck coefficient predictor based on our original tight-binding quantum chemical molecular dynamics program "Colors". We successful applied the new procedure to Pt crystal model. The computed value was in fair agreement with the experimental one. Since our methodology is non-empirical, the prediction of the Seebeck coefficient for other kinds of materials has become possible through this program.

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