Electric and Thermal Transport Calculations through Interface and Applications to Thermoelectric Energy Conversion

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We present the electrical and thermal transport calculations through interface of metallic aluminum and semiconductor silicon materials. The obtained transport results are utilized to find the thermoelectric properties of Seebeck coefficient and figure of merits. We find that the increase of Seebeck coefficients and also the decrease of thermal transport due to the scatterings of electrons and phonons at the nanometer-size interface enhances the efficiency of thermoelectric energy conversion around the Fermi energy. [DOI: 10.1380/ejssnt.2014.115]

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I. INTRODUCTION

Recently much attention has been focused on the construction of energy conversion devices using the nonequilibrium properties, aiming at realizing the smart energy life society. Thermoelectric conversion processes, which transform heat energy into the electric one, become more and more important [1, 2]. To increase the efficiency of thermoelectric conversion, which is determined mainly from the ratio of electric and thermal transport, how to reduce the thermal transport without the reduction of electric current becomes a significant problem.

Since thermoelectric devices are constructed with the thermoelectric materials connected to metallic electrodes, the understanding of thermoelectric properties of the interface is very important. Recent rapid progress of the fabrication technology with nanometer-size precision enables us to construct the composite materials for the realization of high-efficient thermoelectric devices. Although various kinds of materials such as BiTe or PbTe for semiconductors and Cu or Ni for metals have been utilized as good candidates for thermoelectric materials, here we treat Si [3] and Al as typical semiconducting and metallic materials to focus on the microscopic electric and thermal transport calculations through the interface. We show the thermal transport behaviors through the interfaces, thermoelectric properties of Seebeck coefficients, and figure of merits for the high-efficient thermoelectric energy conversion.

II. THEORETICAL METHODS

To treat the thermoelectric properties theoretically, we need to perform both the electric and thermal transport calculations for the system. Although there are a number of calculations methods for electric and thermal transports, here we use mainly the nonequilibrium Green’s function method to treat the nanometer-size transport problems. Below we show briefly their formalisms.

A. Electric Transport

We explain electric transport first. Since the current in nanometer-size materials is influenced by the atomic bonding nature, it is indispensable to use the computational method based on ab initio scheme. Here we use the nonequilibrium Green’s function (NEGF) method [4] combined with ab initio density-functional theory (DFT) in atomically localized basis sets. The procedure is as follows.

First we compute the self-energies $\Sigma_{Al}(\epsilon)$ of aluminium and $\Sigma_{Si}(\epsilon)$ of silicon crystals with use of the results from conventional band calculations. Then we construct the Hamiltonian of the interface region $H_{Al-Si}$ and the retarded ($r$) and advanced ($a$) Green’s functions as

$$G^{ra}(\epsilon) = [\epsilon S_{Al-Si} - H_{Al-Si} - \Sigma_{Al} - \Sigma_{Si} + i\delta]^{-1}, \quad (1)$$
where $S_{Al-Si}$ is the overlap matrix of the localized basis sets in the interface region and $\delta$ is an infinitely small value. The electron density matrix for the present open system is obtained from the integral of
\[
\rho = \frac{1}{2\pi i} \int_{-\infty}^{\infty} G^<(\epsilon)d\epsilon \tag{2}
\]
where the lesser Green’s function $G^<(\epsilon)$ is
\[
G^<(\epsilon) = iG^r(\epsilon)[f_{Al}(\epsilon, T_{Al})\Gamma_{Al}(\epsilon) + f_{Si}(\epsilon, T_{Si})\Gamma_{Si}(\epsilon)]G^a(\epsilon). \tag{3}
\]

**B. Thermal Transport**

Next we explain thermal transport calculations. In the macroscopic materials, the thermal transport is well described by the well-known heat conduction equation [2]. However, in the nanometer-size structures, the use of heat conduction equation is questionable. Instead the methods from the atomistic viewpoints i.e. the molecular dynamics (MD) are needed for thermal transport of such systems.

Here, in parallel with the electric transport calculation, the NEG method for thermal transport [5]. The main different point is that the total Hamiltonian is determined by the dynamical matrix $K$ which consists of force constants of propagating phonons. Then the retarded ($r$) and advanced ($a$) Green’s functions are obtained from
\[
G^{r,a}(\omega) = [\omega^2 M_{Al-Si} - K_{Al-Si} - \Sigma_{Al} - \Sigma_{Si} \mp i\delta]^{-1}. \tag{5}
\]
Here, $M_{Al-Si}$ is the diagonal matrix with a mass of Al or Si at each element. The elements of the dynamical matrix $K_{i\alpha,j\beta}$ are calculated by finite difference of the force $F_{i\alpha}$ respect to $r_{j\beta}$ as
\[
K_{i\alpha,j\beta} = \frac{\partial^2 E}{\partial r_{i\alpha}\partial r_{j\beta}} = \frac{-(F_{i\alpha}(+\Delta R_{j\beta}) - F_{i\alpha}(-\Delta R_{j\beta}))}{2\Delta R_{j\beta}} \tag{6}
\]
with $F_{i\alpha}$ obtained based on the ab initio DFT calculations, which optimize the equilibrium atomic structures including the interface also. Note that $F_{i\alpha}(+\Delta R_{j\beta})$ means the force of i-th atom along the $\alpha$ direction generated by atomic configurations due to displacements $+\Delta R$ for $r_{j\beta}$ from equilibrium positions and is obtained from a derivative of the total energy of the system $E$. We take a displacement $\Delta R = 2 \times 10^{-4} \AA$ here.

The thermal current $J_{th}$ of the system is expressed as
\[
J_{th} = \int_0^{\infty} \frac{e^{\omega/k_B T_{Al-Si}}}{k_B T_{Al-Si}} T_{ph}(\omega)d\omega, \tag{7}
\]
where $\eta(\omega; T_{Al-Si}) = 1/(e^{\hbar \omega/k_B T_{Al-Si}} - 1)$ are the Bose-Einstein distribution functions of equilibrium phonons with energy $\hbar \omega$ for aluminum and silicon sides. $T_{ph}(\omega)$ is the transmission function for phonon transport by
\[
T_{ph}(\omega) = \frac{d J_{th}}{dT} = \frac{k_B}{2\pi} \int_0^{\infty} \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{k_B T \hbar \omega}}{e^{k_B T \hbar \omega} - 1} T_{ph}(\omega)d\omega. \tag{9}
\]

**III. RESULTS AND DISCUSSION**

Here we show the electric and thermal transport through the Al-Si interface and present its thermoelectric properties. We use Al (100) and Si (100) semi-infinite crystals with an interface. The equilibrium atomic positions are determined by the DFT calculations with structural relaxations. The electric and thermal currents flow in the (100) direction.

**A. Electric Transport through Al-Si Interface**

Figure 1 displays $\rho(\mathbf{r})$ around the Al-Si interface (left) and the electric conductance $G$ as a function of electron energy $\epsilon$ at $T = 0$ (right). Note that $G(T = 0, \epsilon)$ corresponds to the electric transmission $T_{el}(\epsilon) = \frac{d J_{el}}{dT} = \int G^r(\epsilon)\Gamma_{Al}(\epsilon)G^a(\epsilon)\Gamma_{Si}(\epsilon)d\epsilon$ in units of $2e^2/h$ due to the relation of $-\partial f(\epsilon, T = 0)/\partial \epsilon = \delta(\epsilon - E_F)$. Since the aluminum is a metal and the silicon is a semiconductor material, we see that strong covalent bondings are formed in Si while the electrons are spread out in Al.

The electric conductance shows smooth behavior in the valence band smaller than $\approx -1$ eV and in the conduction band larger than $\approx 1.2$ eV. However, around the band gap region, we see that the electric transport properties are strongly affected to give spiky structures. Apparently

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
these structures appear due to the effects from the interface. Since the rapid change of electric transport produces large thermopower through the Seebeck coefficients, they contribute to the increase of thermoelectric properties significantly.

B. Thermal Transport through Al-Si Interface

In Fig. 2, we show the thermal properties around the interface. Let us see the nonequilibrium thermal properties first. The left panel of Fig. 2 shows the local temperature distribution obtained from the nonequilibrium molecular dynamics (MD) simulations for two materials. Here we use simply the Lennard-Jones interatomic potentials $U_{i,j} = 4 \varepsilon \left\{ (\sigma/r)^{12} - (\sigma/r)^{6} \right\}$ for MD simulations with parameters of $\varepsilon = \sigma = M = 1$ for one side and $\varepsilon = 2, \sigma = 1, M = 1/2$ for the other side. We see that the local temperatures decrease almost linearly as a function of distance inside the materials from high to low temperatures. This behavior is well-known as Fourier’s law in classical transport. However, we see that the local temperature changes rapidly around the interface region. The jump of local temperature is due to the Kapitza resistance (discovered historically at interfaces between helium and solids at low temperature) and is analyzed e.g. by the diffuse mismatch model (DMM) [6] where all the phonons are assumed to be diffusively scattered at the interface. Around room temperature, the phonon scattering plays important roles. The present MD simulations clearly show that we must treat the thermal properties and transport around the interface region very carefully, taking the precise atomic structures quantum mechanically into account.

The right panel of Fig. 2 shows the temperature dependence of thermal conductances of bulk Al, bulk Si, and Al-Si system including the interface by the nonequilibrium Green’s function method. We see that, although the thermal conductances show similar behaviors for metallic Al and semiconductor Si materials, it reduces significantly for Al-Si system with the interface. This reduction is apparently due to the scatterings of phonons at the interface region, which contributes to an increase of the efficiency of thermoelectric energy conversion.
electric conductance is influenced significantly by the interface. Here we note that in the bulk materials of Al and Si, $ZT$ is much smaller than 0.1; $ZT \ll 0.1$ [2].

To study the thermoelectric properties more, we show in Fig. 3 (b) the temperature dependence of the Seebeck coefficient $S$ obtained from the Mott’s formula: $S = -\left(\pi^2/3\right)(k_B T/e) \left|\partial \ln (G(T, \epsilon))/\partial \epsilon\right|_{\epsilon=E_F}$. Note that $S$ becomes both positive and negative, depending on the nature of carriers. Here we show the absolute values.

In general, $S$ becomes very small for metals ($\sim 0–1 \mu V/K$) and large for semiconductors (larger than 100 $\mu V/K$ for Si [7]). In the present interface we see that fairly large values of $S = 20 \mu V/K$ are obtained at room temperature at $E_F = -0.35 \text{ eV}$, which increase $ZT$ significantly as shown in Fig. 3 (c) where the temperature dependence of $ZT$ is shown. We note that both the large values of $S$ which comes from the rapid change of $G$ and the small values of $\kappa_e$ contribute to the appearance of large values of $ZT$. This shows that the efficiency of thermoelectric energy conversion enhances due to the effects of the interface.

IV. CONCLUSION

In conclusion, we perform electric and thermal transport calculations of metallic Al and semiconductor Si materials with interface towards the applications to high-efficient thermoelectric energy conversion. We found that, due to the scatterings of electrons and phonons at the interface, the increase of Seebeck coefficients and the decrease of thermal transport contribute to an increase of the efficiency of thermoelectric energy conversion around the Fermi energy.

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