First-principles analysis on Seebeck coefficient in zinc oxide nanowires for thermoelectric devices

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Abstract. The Seebeck coefficient of ZnO<sub>0001</sub> nanowires was simulated on the basis of first-principles calculation, to discuss the potential for future application to thermoelectric devices. Simulation procedure by means of the electronic band structure with one-dimensional periodic boundary condition was presented, and dependences of the Seebeck coefficient on temperature and carrier concentration have been investigated for many kinds of n- or p-doped ZnO<sub>0001</sub> nanowire models with 1.00–2.65 nm diameter. For the direct band-gap semiconducting models, a magnitude of the Seebeck coefficient increases gradually as temperature rises in the p-doped state, and a significant effect of miniaturization to nanowire on the Seebeck coefficient has been brought out, such as about 1000 μV/K in the p-doped state and –820 μV/K in the n-doped state for the (ZnO)<sub>24</sub> nanowire model with 1 × 10<sup>17</sup> cm<sup>–3</sup> carrier concentration at room temperature. Similar characteristics of the Seebeck coefficient were observed for some indirect band-gap semiconducting models. At the end of this paper, the simulation was extended to the no band-gap conducting models with some modification.

1. Introduction

Zinc oxide (ZnO) is an important semiconducting material with excellent performance in optics, electronics, energy science, and so forth [1-7]. Thermoelectric properties of ZnO-based materials have been investigated in terms of thermoelectric power generation at high temperature, by introduction of microstructure, nanovoid or solid solution with other metal oxides to improve thermoelectric performance [1-3]. On the other hand, it has been reported both experimentally and theoretically that miniaturization to lower-dimensional materials at nanoscale is one of promising techniques to enhance energy conversion efficiency [8,9]. From the viewpoint of electronic state, density of state (DOS), g(ε), of thermoelectric materials is radically affected by the dimension reduction, leading to the improvement of thermoelectric performance.

The detailed electronic states of wurtzite-ZnO nanowires with ⟨0001⟩ orientation have been reported in the previous study [10]; according to the difference in wall structure, ZnO⟨0001⟩ nanowires can be divided into three groups by their conductivities such as no band-gap conducting models, direct band-gap semiconducting models, and indirect band-gap semiconducting models. As expected, different characteristics of thermoelectricity should be observed in response to the
classification of conductivity or electronic state in these ZnO nanowires. In this study, the Seebeck coefficient, one of the contributing terms to the power factor in the thermoelectric figure of merit, of ZnO(0001) nanowires was simulated on the basis of the first-principles calculation of model structures; particularly, carrier concentration and temperature dependences of the Seebeck coefficient were discussed to estimate the potential for future application to thermoelectric devices.

2. Simulation method

2.1. First-principles calculation

Electronic band structures of the one-dimensional periodic boundary models for wurtzite-ZnO nanowires have been calculated by VASP program package [11,12] based on the density functional theory (DFT) [13]. For the DFT exchange-correlation interaction, the generalized-gradient approximation method was used with the Perdew-Wang (PW91) functional [14,15]. We adopted the three-dimensional supercell approximation technique with ultrasoft pseudopotentials [16]. The cutoff energy for wave functions of electrons with plane-wave expansion was set at 40 Ry (544 eV) for bulk ZnO crystal and 30 Ry (408 eV) for ZnO nanowire models.

ZnO nanowire models have been devised in the previous papers [10,17], as shown in figure 1. The list of wurtzite-ZnO(0001) nanowire models is tabulated in table 1. These models were devised by cutting out a fragment with one-dimensional periodic boundary condition from the optimized bulk ZnO. The direction of the fragment with the one-dimensional periodic boundary is set to [0001] and can be defined as the longitudinal direction of ZnO nanowire. A periodic boundary condition along the transverse or perpendicular direction to the nanowire in the three-dimensional hexagonal supercell was given by inserting sufficient space between nanowires with a large cell parameter. On the condition that sufficient space in the ZnO nanowire model disturbs the interaction between nanowires, the electronic band structure of the ZnO nanowire model can be reduced to be one dimensional, which is dependent on only one reciprocal coordinate, \( k_z \).

The characteristics of electronic state for each nanowire group listed in table 1 have been discussed in the previous study [10]. We can find some common features of band structure among the nanowire models belonging to the same group. Figure 2 shows examples of band structure for each nanowire group.

![Figure 1. Top views of wurtzite-ZnO(0001) nanowire models, (ZnO)\(n\).](image-url)
Table 1. Structural parameters of wurtzite-ZnO(0001) nanowire models and their hexagonal unit cells

| Model     | Wire radius $R$ (Å) | Wire volume per unit cell $V$ (Å$^3$) | Cell parameter (Å) |
|-----------|---------------------|--------------------------------------|--------------------|
|           |                     |                                      | $L_{//}$ | $L_{z}$ |
| Direct band-gap |                   |                                      |         |        |
| (ZnO)$_{24}$ | 5.019               | 394.3                                | 22.000  | 5.280  |
| (ZnO)$_{37}$ | 6.383               | 665.3                                | 25.000  | 5.280  |
| (ZnO)$_{44}$ | 8.266               | 1035.0                               | 27.000  | 5.280  |
| (ZnO)$_{53}$ | 10.034              | 1453.9                               | 30.000  | 5.280  |
| (ZnO)$_{66}$ | 11.534              | 1971.4                               | 33.000  | 5.280  |
| (ZnO)$_{121}$ | 13.272              | 2538.1                               | 37.000  | 5.280  |
| Indirect band-gap |          |                                      |         |        |
| (ZnO)$_{25}$ | 5.690               | 443.6                                | 22.000  | 5.280  |
| (ZnO)$_{39}$ | 7.586               | 763.9                                | 25.000  | 5.280  |
| (ZnO)$_{40}$ | 7.586               | 763.9                                | 25.000  | 5.280  |
| No band-gap |                     |                                      |         |        |
| (ZnO)$_{31}$ | 6.570               | 591.4                                | 22.000  | 5.280  |
| (ZnO)$_{45}$ | 8.266               | 911.8                                | 25.000  | 5.280  |
| (ZnO)$_{46}$ | 8.266               | 911.8                                | 25.000  | 5.280  |

2.2. Seebeck coefficient

The Seebeck coefficient $S$ is given by the ratio of electromotive force $\tilde{E}$ to temperature gradient $\nabla T$ incorporated implicitly in the Boltzmann transport equation [18,19]. In the stationary state, velocity distribution function of carriers $f$ in semiconductor should be derived from the Boltzmann transport equation by use of relaxation time $\tau$ as

$$f(\varepsilon) - f_0(\varepsilon) = \tau(\varepsilon)\tilde{v}(\varepsilon)\left(df_0/d\varepsilon\right)\{\varepsilon\tilde{E} + [(\varepsilon - \varepsilon_F)/T]\nabla T\}, \quad (1)$$

where $e$ is the elementary charge, $\tilde{v}$ is carrier velocity, $\varepsilon_F$ is the Fermi energy, and $f_0$ is the Fermi-Dirac distribution defined by

$$f_0(\varepsilon) = \left\{\exp[(\varepsilon - \varepsilon_F)/k_BT] + 1\right\}^{-1} \quad (2)$$

with the Boltzmann constant $k_B$. Then, $S$ can be evaluated from the information from band structure of the material in terms of integrals including DOS with respect to energy $\varepsilon$ by

$$S = -(1/eT)\left\{\int g(\varepsilon)\tau(\varepsilon)\alpha^2(\varepsilon)(df_0/d\varepsilon)d\varepsilon \right\} \int g(\varepsilon)\tau(\varepsilon)\alpha^2(\varepsilon)(df_0/d\varepsilon)d\varepsilon \right\} - \varepsilon_F \right\}, \quad (3)$$

where interval of the integrals corresponds to the region of carrier occupation. All physical properties in (3) except for the relaxation time can be easily determined from the first-principles electronic state, because the amount of carrier velocity $\nu$ can be evaluated from the slope of each band energy curve. At the case that the relaxation time is constant regardless of $\varepsilon$, the effect of $\tau$ on $S$ is canceled.
Carrier doping should be considered for the application to devices, and we have presented the original procedure to represent the n- or p-doped state in semiconductors [20,21]. An excess or lack of electrons by as much as one particle per unit cell in order to carry out regular first-principles calculations for the n- or p-type semiconductor state should lead to an enormous overestimation of carrier concentration as much as the $10^{21}$ cm$^{-3}$ order for our ZnO nanowire models. In practical n- or p-type ZnO nanowires, the total number of carriers per unit cell, $\delta = nV$, must be a few orders less than 1, where $n$ is the carrier concentration and $V$ is the volume of ZnO nanowire in the unit cell. Under the condition that a small amount of carrier occupation does not cause significant change in the band structure, $\delta$ can be given by an appropriate shift of $\varepsilon_k$ as

$$\delta = \int_{CB} 2g(\varepsilon)f_0(\varepsilon)d\varepsilon = 2\sum_{j=CB} w_{k_j} f_0(\varepsilon_{j,k})$$

in the n-type carrier occupation on the conduction band (CB) or
\[ \delta = \int_{V_B} 2g(\varepsilon)[1 - f_0(\varepsilon)]d\varepsilon = 2 \sum_{j \in V_B} \sum_{k_z} w_{k_z} [1 - f_0(\varepsilon_{j,k_z})] \]  

(5)

in the p-type carrier occupation on the valence band (VB) with temperature \( T \), where \( \varepsilon_{j,k_z} \) is the intrinsic-semiconductor-state band energy of the \( j \)th subband at the \( k_z \) point, and \( w_{k_z} \) is the k-point weight for \( k_z \). In practice, we first set \( \delta \) to an appropriate small constant a few orders less than 1, and then solve \( \varepsilon_0 \) in n-type and p-type carrier occupations according to (4) and (5), respectively. The sampling for \( w_{k_z} \) is performed using the Newton-Cotes formula [22] with 29 \( k_z \) points along the reciprocal longitudinal path, and it can be applied to the evaluation of the Seebeck coefficient \( S \) in (3) as follows,

\[ S = -\frac{1}{eT} \left\{ \frac{\sum_{j} \sum_{k_z} w_{k_z} \varepsilon_{j,k_z}^2 (\varepsilon_{j,k_z}) \frac{df_0(\varepsilon_{j,k_z})}{d\varepsilon} \int \sum_{j} \sum_{k_z} w_{k_z} \varepsilon_{j,k_z}^2 (\varepsilon_{j,k_z}) \frac{df_0(\varepsilon_{j,k_z})}{d\varepsilon}}{\int \sum_{j} \sum_{k_z} w_{k_z} \varepsilon_{j,k_z}^2 (\varepsilon_{j,k_z}) \frac{df_0(\varepsilon_{j,k_z})}{d\varepsilon}} - \varepsilon_f \right\}, \]  

(6)

where \( j \)th subbands belong to CB in the n-doped state or VB in the p-doped state, under the condition that the relaxation time is constant regardless of energy \( \varepsilon \).

3. Results and discussion

3.1. Direct band-gap semiconducting ZnO nanowires

Figure 3 shows temperature and carrier concentration dependences of the calculated Seebeck coefficients for the (ZnO)\textsubscript{24} and (ZnO)\textsubscript{121} direct band-gap nanowire models, in the range from −200 to 300 °C. The results satisfy the well-known fundamental features of Seebeck coefficient for semiconductors [18]: (i) \( S \) should be positive in the p-doped state and negative in the n-doped state, and (ii) the absolute value of \( S \) is reduced as the carrier concentration increases.

Regarding to temperature dependence for each carrier concentration, \( S \) increases gradually as temperature rises in the p-doped state, whereas \( S \) almost keeps a fixed value regardless of temperature more than −100 °C in the n-doped state. Actually, even at high temperature, most all of carrier electrons should be distributed only on the lowest CB subband, which is located far from other higher CB subbands as shown in figure 2(a). It is considered that no redistribution of carrier electrons would suppress temperature dependence of the Seebeck coefficient for one-dimensional nanomaterials.

![Figure 3. Temperature and carrier concentration dependences of the calculated Seebeck coefficients for the direct band-gap models. Solid and dashed lines denote the (ZnO)\textsubscript{24} and (ZnO)\textsubscript{121} models, respectively. Circle, square, and triangle plots respectively mean the carrier concentration of \( 1 \times 10^{19} \), \( 1 \times 10^{18} \), and \( 1 \times 10^{17} \) cm\(^{-3} \).](image)
The same trend in the behavior of temperature dependence was observed for all direct band-gap models. As tabulated in table 2, it has been also clarified that the absolute values of \( S \) are raised as the wire diameter decreases in both of n- and p-doped states. For the (ZnO)\(_{24}\) model, \( S \) expands to as much as 1000 \( \mu \)V/K in the p-doped state and –820 \( \mu \)V/K in the n-doped state, respectively, with the carrier concentration of \( 1 \times 10^{17} \) cm\(^{-3}\) at room temperature. Thus, significant effect of miniaturization to nanowire on the Seebeck coefficient can be displayed.

### Table 2. Calculated Seebeck coefficients (\( \mu V/K \)) for the direct band-gap models with the carrier concentration of \( 1 \times 10^{17} \) cm\(^{-3}\).

| Model       | Temperature |
|-------------|-------------|
|             | –50 °C      | 20 °C | 100 °C | 200 °C |
| p-type      |             |       |        |        |
| (ZnO)\(_{24}\) | 989         | 1010  | 1031   | 1053   |
| (ZnO)\(_{37}\) | 1005       | 1033  | 1050   | 1064   |
| (ZnO)\(_{54}\) | 889         | 927   | 958    | 985    |
| (ZnO)\(_{73}\) | 834         | 869   | 903    | 935    |
| (ZnO)\(_{96}\) | 806         | 841   | 875    | 909    |
| (ZnO)\(_{121}\) | 794        | 828   | 858    | 886    |
| n-type      |             |       |        |        |
| (ZnO)\(_{24}\) | –820        | –819  | –819   | –825   |
| (ZnO)\(_{37}\) | –776        | –774  | –774   | –778   |
| (ZnO)\(_{54}\) | –737        | –736  | –735   | –739   |
| (ZnO)\(_{73}\) | –708        | –707  | –706   | –708   |
| (ZnO)\(_{96}\) | –681        | –681  | –680   | –681   |
| (ZnO)\(_{121}\) | –659        | –660  | –658   | –659   |

3.2. Indirect band-gap semiconducting ZnO nanowires

Temperature and carrier concentration dependences of the calculated Seebeck coefficients for the (ZnO)\(_{25}\) and (ZnO)\(_{39}\) indirect band-gap nanowire models are shown in figure 4. For the (ZnO)\(_{25}\) and (ZnO)\(_{39}\) models shown in table 3, similar characteristics of the Seebeck coefficient as the direct band-gap nanowire models were observed; namely, \( S \) increases gradually as temperature rises in the p-doped state and does not change regardless of temperature more than –100 °C in the n-doped state, respectively. On the other hand, for the (ZnO)\(_{39}\) model, \( S \) is independent of temperature more than 0 °C in the p-doped state as well as the n-doped state.

Difference in the electronic structure between the (ZnO)\(_{25}\) and (ZnO)\(_{39}\) models can be clearly found in figures 2(b) and 2(c). For the (ZnO)\(_{39}\) model, the highest VB subband and the second highest VB subbands in double degeneracy are completely isolated from other lower VB subbands, and therefore, the energy range of hole redistribution due to temperature change should be restricted to these three highest VB subbands. The behavior of the Seebeck coefficient for the p-doped (ZnO)\(_{39}\) model strongly supports the consideration discussed above that temperature dependence of the Seebeck coefficient for one-dimensional nanomaterials would not be clearly observed unless the carrier redistribution occurs adequately.
Figure 4. Temperature and carrier concentration dependences of the calculated Seebeck coefficients for the indirect band-gap models. Solid and dashed lines denote the \((\text{ZnO})_{25}\) and \((\text{ZnO})_{39}\) models, respectively. Circle, square, and triangle plots respectively mean the carrier concentration of \(1 \times 10^{19}\), \(1 \times 10^{18}\), and \(1 \times 10^{17}\) cm\(^{-3}\).

Table 3. Calculated Seebeck coefficients (\(\mu\text{V/K}\)) for the indirect band-gap models with the carrier concentration of \(1 \times 10^{17}\) cm\(^{-3}\).

| Model  | Temperature   |
|--------|---------------|
|        | \(-50 ^\circ\text{C}\) | \(20 ^\circ\text{C}\) | \(100 ^\circ\text{C}\) | \(200 ^\circ\text{C}\) |
| p-type | \((\text{ZnO})_{25}\) | 1004 | 1024 | 1043 | 1063 |
|        | \((\text{ZnO})_{39}\) | 974 | 982 | 985 | 985 |
|        | \((\text{ZnO})_{40}\) | 972 | 979 | 994 | 1021 |
| n-type | \((\text{ZnO})_{25}\) | \(-810\) | \(-809\) | \(-809\) | \(-815\) |
|        | \((\text{ZnO})_{39}\) | \(-811\) | \(-809\) | \(-809\) | \(-813\) |
|        | \((\text{ZnO})_{40}\) | \(-764\) | \(-762\) | \(-762\) | \(-766\) |

3.3. No band-gap conducting ZnO nanowires

To apply the simulation method in this paper to conducting systems, (4) and (5) can be modified by using a general form of electron distribution [23] as follows,

\[
\delta = \pm \left[ 2g(e)f_{0}(e)d\varepsilon - N \right] = \pm \left[ 2\sum_{\Delta k} \sum_{i} w_{i} f_{0}(\varepsilon_{k,i}) - N \right],
\]

where \(N\) is the total number of electrons in the system, and plus-minus sign means plus for n-doped state or minus for p-doped state. In this study, the Fermi energy \(\varepsilon_{F}\) was determined according to (7) for each condition, and then the value of \(S\) was evaluated by using (6) under the condition that the relaxation time is constant. Practically, the effect of relaxation time on the Seebeck coefficient is
relatively small for the semiconducting material, because the effective \( \tau(\epsilon) \) has a small overlap with the derivative of the Fermi-Dirac distribution \( df_0/d\epsilon \). On the contrary, the energy dependence of \( \tau(\epsilon) \) in the vicinity of the Fermi energy will affect the Seebeck coefficient significantly in the case of metallic conducting material. Therefore, the relaxation time should be taken into consideration for the quantitative analysis on the Seebeck coefficient for the conducting material, but the simulation by using (6) is available for easy evaluation.

Figure 5 shows temperature dependence of the calculated Seebeck coefficients for the (ZnO)\(_{31}\), (ZnO)\(_{45}\), and (ZnO)\(_{46}\) no band-gap nanowire models. A magnitude of \( S \) for the conducting material is much smaller than that for the semiconducting one as is well-known, and plus/minus in \( S \) does not correspond to p-/n-doping. In contrast to the semiconducting material, a large amount of carriers in the conducting one exists in the quite vicinity of the Fermi energy. Accordingly, the characteristics of the Seebeck coefficient for the conducting material is very sensitive according to the small difference in the electronic structure.

![Figure 5. Temperature and doped state dependences of the calculated Seebeck coefficients for the no band-gap models.](image)

4. Summery

In this paper, the Seebeck coefficient of ZnO(0001) nanowires was simulated on the basis of first-principles calculation. Simulation procedure by means of the electronic band structure with one-dimensional periodic boundary condition was presented, and dependences of the Seebeck coefficient on temperature and carrier concentration have been demonstrated for many kinds of n- or p-doped ZnO(0001) nanowire models with 1.00–2.65 nm diameter [10,17]. For the direct band-gap semiconducting models, a magnitude of the Seebeck coefficient increases gradually as temperature rises in the p-doped state, and a significant effect of miniaturization to nanowire on the Seebeck coefficient has been brought out, such as about 1000 \( \mu \)V/K in the p-doped state and –820 \( \mu \)V/K in the n-doped state for the (ZnO)\(_{31}\) nanowire model with \( 1 \times 10^{17} \) cm\(^{-3} \) carrier concentration at room temperature. Similar characteristics of the Seebeck coefficient were observed for some indirect band-gap semiconducting models. The simulation was extended to the no band-gap conducting models with some modification for determination of the Fermi energy [23], and much smaller values of the Seebeck coefficient were obtained, as compared with the semiconducting models.
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