Chapter 15 Generic Model of Bulk Silicon and Nanowires

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So far we have studied semiclassical theories for electrons and phonons for bulk and low-dimensional structures (quantum well, nanowires, etc.). Silicon (Si) is considered as a future potential thermoelectric material due to its abundance, nontoxicity, large processing infrastructure for low cost and high-yield in addition to its good electronic transport properties. However, bulk Si has a high thermal conductivity of \( \sim 150 \text{ W/mK} \), leading to a poor thermoelectric performance \( (ZT \approx 0.01) \). Si nanowires have Seebeck coefficient and electrical conductivity that are comparable to bulk Si, but those with diameters of about 30 nm exhibit 100-fold reduction in thermal conductivity, yielding \( ZT = 0.6 \) at room temperature (Hochbaum et al. 2008)[1]. In spite of a remarkable achievement on thermal conductivity with nanowires, there are a remaining question as to why electronic transport properties with nanowires did not show better performance than those in bulk Si, as expected from the work of Hicks and Dresselhaus (1993)[2, 3]. According to the literature, it seems difficult to determine electron scattering mechanisms for nanowires. Assuming a constant scattering rate [4, 5] or using experimental values (Lin and Dresselhaus, 2003) [6], whereas phonon scattering mechanisms are given much attention. Actually, Monte Carlo and Ab initio simulations of detailed electronic transport for Si nanowires including electron scattering were reported by Ramayya et al. (2012) [7] and Neophytou and Kosina (2011) [8], respectively, wherein \( ZT \) does not show much enhancement with decreasing nanowire diameter. However, these give detailed information on electronic transport in nanowires, which would be valuable data for the present work. In the previous chapters, it was shown that transport properties for both bulk and nanowires give rise to changes only in their electron density of states. Therefore, we first develop a nonparabolic two-band Kane model for bulk Si in terms of the density of states by comparing the computed results with experimental data, and try to extend it from bulk to
nanowire by just switching the electronic density of states. We wish to see the realistic electronic transport behaviors for nanowires. The validity for this attempt is open to future work.

15.1 Electron Density of States for Bulk and Nanowires

Density of States

From Equation (12.105), the nonparabolic density of states for bulk Si in terms of the reduced energy is given as

\[
g_{\text{bulk}}(E^*) = \frac{N_v}{2\pi^2} \left( \frac{2m_d^*}{\hbar^2} \right)^{\frac{3}{2}} (k_B T)^{\frac{1}{2}} \left( E^* + \frac{E^* E_G^*}{E_G^*} \right) \left( 1 + \frac{2E^*}{E_G^*} \right) \tag{15.1}
\]

where \( E^* \) is the reduced energy \( (E^* = E/k_B T) \) and \( E_G^* \) is the reduced bandgap \( (E_G^* = E_G/k_B T) \). \( N_v \) is the degeneracy of valleys and \( m_d^* \) is the density-of-states effective mass. \( k_B \) is the Boltzmann constant, \( \hbar \) is the reduced Planck constant and \( T \) is the absolute temperature. From Equation (14.28), the 1D density of states for nanowires is given as

\[
g_{1D}(E^*) = \frac{N_v}{\pi d^2} \left( \frac{2m_d^*}{\hbar^2 k_B T} \right)^{\frac{1}{2}} \left( E^* + \frac{E^* E_G^*}{E_G^*} \right)^{-\frac{1}{2}} \left( 1 + \frac{2E^*}{E_G^*} \right) \tag{15.2}
\]

where \( d \) is the nanowire diameter.

15.2 Carrier Concentrations for Two-band Model

Bulk

Two-band model takes account of a conduction band and a valence band. The electron and hole concentrations for bulk are given as
\[ n_e = k_B T \int_0^\infty g(E^*) f_0(E^*) dE^* = k_B T \int_0^\infty \frac{g(E^*)}{e^{(E^*-E_F^*)} + 1} dE^* \quad (15.3) \]

\[ n_h = k_B T \int_0^\infty g(E^*) f_0(E^*) dE^* = k_B T \int_0^\infty \frac{g(E^*)}{e^{(E^*+E_G^*+E_F^*)} + 1} dE^* \quad (15.4) \]

where \( E_F^* \) is the reduced Fermi energy \( (E_F^* = E_F / k_B T) \).

**Nanowires**

You may see Section 12.5 for the two-band model. For nanowires, the reduced lowest subband energy \( E_0^* \) of Equation (14.27) should be included. From Equation (15.3), the electron concentration for nanowires is expressed as

\[ n_{1D,e} = k_B T \int_0^\infty g_{1D,e}(E^*) f_0(E^*) dE^* = k_B T \int_0^\infty \frac{g_{1D,e}(E^*)}{e^{(E^*-E_F^*)} + 1} dE^* \quad (15.5) \]

where the reduced lowest subband energy is \( E_0^* = E_0 / k_B T \). We consider only the lowest subband, an assumption that is widely used in literature. Taking account of the coordinate in conjunction with the bandgap for the valence band, the hole concentration with the subband for nanowires is similarly expressed as

\[ n_{1D,h} = k_B T \int_0^\infty g_{1D,h}(E^*) f_0(E^*) dE^* = k_B T \int_0^\infty \frac{g_{1D,h}(E^*)}{e^{(E^*+E_G^*+E_F^*)} + 1} dE^* \quad (15.6) \]

**Bipolar Effect and Fermi Energy**

It is usually a good assumption that all doped electrons (or holes in \( p \)-type) become free without being accompanied by holes (or electrons in \( p \)-type) and easily move to the conduction band contributing to the electrical conductivity. However, sometimes electrons of atoms in the valence band become free with being accompanied by holes and jump to the conduction band across the bandgap if the energy is high enough due to elevated temperature. This process increases the number of electrons more than those of the doped, which is called bipolar effect. The bipolar
effect produces more electrons at high temperatures. So it may be beneficial or may not. Usually increasing the number of electrons may cause a dual effect: increasing the electrical conductivity (good), and increasing the scattering rate and decreasing the Seebeck coefficient (no good). The doping concentration $n_d$ is mathematically the absolute difference of between the electron concentration and hole concentration because the electrons are negative while holes are positive. Physically they are added by the bipolar effect. Hence, we can set the equation as

$$n_d = n_e - n_h$$

If the doped concentration and temperature are given, the Fermi energy can be exclusively calculated from this equation.

### 15.3 Electron Transport Properties for Bulk and Nanowires

#### Electrical Conductivity

In a similar manner to Section 12.2.2 with Equation (12.107), the generic electrical conductivity for bulk and nanowires is expressed as

$$\sigma = \frac{2e^2k_BT}{3m_c^*} \int_0^\infty g(E^*)\tau\left(-\frac{\partial f_0}{\partial E^*}\right)\left(E^* + \frac{E^{*2}}{E_G^*}\right)^2\left(1 + \frac{2E^*}{E_G^*}\right)^{-2} dE^*$$

where $\tau$ is the electron relaxation time, $e$ is the electron charge and $m_c^*$ is the conductivity effective mass. Here the term “generic” means for both bulk and nanowires. Since $\sigma = ne\mu_x$, the generic electron mobility for bulk and nanowires is expressed as
\[ \mu_x = \frac{2e^2k_BT}{3m^*_c} \int_0^\infty \frac{g(E^*)\tau \left( -\frac{\partial f_0}{\partial E^*} \right) \left( E^* + \frac{E^{*2}}{E_G^*} \right) \left( 1 + \frac{2E^{*2}}{E_G^*} \right)^{-1} dE^*}{eke^2 \int_0^\infty \frac{g(E^*)}{e^{(E^* - E_F^*)} + 1} dE^*} \]  

(15.9)

Note that the electrical conductivity and mobility are expressed in terms of the density of states in the integrands.

**Seebeck Coefficient**

In a similar manner to Section 12.2.3, the *generic Seebeck coefficient* for bulk and nanowires is expressed as

\[
\alpha = -\frac{k_B}{e} \left[ \int_0^\infty g(E^*)E^*\tau \left( -\frac{\partial f_0}{\partial E^*} \right) \left( E^* + \frac{E^{*2}}{E_G^*} \right) \left( 1 + \frac{2E^{*2}}{E_G^*} \right)^{-1} dE^* \right] \]  

(15.10)

In case of 1D nanowires, the \( E_F^* \) in Equation (15.10) should be replaced by \( E_F^* - E_0^* \) for the Seebeck coefficient of electrons.

**Electronic Thermal Conductivity**

In a similar manner to Section 12.2.4, the *generic electronic thermal conductivity* is expressed as

\[ k_e = \sigma TL_0 \]  

(15.11)

where
which is known as Lorenz number.

15.4 Electron Scattering Mechanisms

This topic was discussed in Section 12.4. Electron scattering in nanowires is very important and challenging, with a scarcity in literature, while that in bulk materials has relatively more theoretical and experimental reports. Also, many studies on phonon scattering in nanowires can be found in the literature. The three fundamental electron scattering mechanisms are used here, which are the acoustic phonon, ionized impurity and polar optical phonon scattering mechanisms. Nonparabolicity and density of states are implemented into the model. Note that the density of states remains in the expressions for substitution between bulk and nanowires.

15.4.1 Acoustic-Phonon Scattering

The generic relaxation time for acoustic-phonon scattering is expressed as [9, 10]

$$\tau_a = \frac{\hbar v_s^2 d_m N_v}{\pi \Phi_a^2 k_B T g(E^*) [(1 - A_a)^2 - B_a]}$$

where
\[ A_a = \frac{E_r^* (1 - K_a)}{1 + 2E_r^*} \]

\[ B_a = \frac{8 E_r^* (1 + E_r^*) K_a}{3 \left( 1 + 2E_r^* \right)^2} \]

where \( d_m \) is the mass density, \( \Phi_a \) is the acoustic deformation potential, \( v_s \) is the velocity of sound (see Equation (13.45)), \( K_a \) is the ratio of the acoustic deformation potential for the valence and conduction bands \( \Phi_{av}/\Phi_{ac} \), which is often assumed unity. Note that the relaxation time is expressed in terms of the density of states.

15.4.2 Ionized Impurity Scattering

The generic relaxation time for ionized impurity scattering is given as [11, 12]

\[ \tau_I = \frac{(2m_a^*)^{\frac{1}{2}} \epsilon_0^{\frac{1}{2}} (k_B T)^{\frac{3}{2}} \left( E^* + \frac{E_r^*}{E_G} \right)^{\frac{2}{3}} \left( 1 + \frac{2E_r^*}{E_G} \right)^{-1}}{\pi N_I (Ze^2)^2 \left( \ln(1 + b) - \frac{b}{1 + b} \right)} \quad (15.14) \]

where

\[ r_0 = \left( \frac{1}{N_0 \epsilon_0} \right) \int_0^\infty \left( - \frac{\partial f_0}{\partial E^*} \right) g(E^*) dE^* \quad (15.15) \]

\[ k_F = \left( \frac{2m_d^* k_B T}{\hbar^2} \left( E^* + \frac{E_r^*}{E_G} \right) \right)^{\frac{1}{2}} \quad (15.16) \]
where $Ze$ is the vacancy charge, $\varepsilon_o$ is the static permittivity, where the units are same as the permittivity of vacuum $\varepsilon_0$, $N_I$ is the ionized impurity concentration, $r_0$ is the screening radius, and $k_F$ is the Fermi wavevector. Equation (15.14) is known as *Brooks-Herring formula*. Note that the screening radius is expressed in terms of the density of states. So the scattering is affected by the change of the density of states. In fact, the ionized impurities scattering is a dominant mechanism for bulk Si (will discuss later).

**Screening effect**

In the absence of any potential, we may assume that the free electrons are uniformly distributed in a semiconductor. However, in regions where potential discontinuities occur, the free electrons collect or are removed in accordance with the sign of the potential discontinuity. Ionized impurities cause this *screening effect*. Nag (1980)[13]

### 15.4.3 Polar Optical Phonon Scattering

The generic relaxation time for *optical phonon scattering* is expressed as [14, 15]

$$
\tau_{po} = \frac{8\pi\hbar^2 \left(E^* + \frac{E^{*2}}{E_G^*}\right)^{\frac{1}{2}} \left(1 + \frac{2E^{*}}{E_G^*}\right)^{-1}}{e^2(2m_d^*k_B T)^{\frac{1}{2}}(\varepsilon^{-1}_\infty - \varepsilon^{-1}_o)G_{po}}
$$

where
\[ G_{po} = 1 - \delta \cdot \ln \left( 1 + \frac{1}{\delta} \right) - \frac{2 E^*}{E_G} \left( 1 + \frac{E^*}{E_G} \right) \left( 1 - 2\delta + 2\delta^2 \ln \left( 1 + \frac{1}{\delta} \right) \right) \]  
\[ (15.19) \]

\[ r_{0,\infty} = \left( \frac{1}{N_v \varepsilon_\infty} \int_0^\infty \left( -\frac{\partial f_0}{\partial E^*} \right) g(E^*) dE^* \right)^{\frac{1}{2}} \]  
\[ (15.20) \]

\[ k_F = \left( \frac{2m^*_d k_B T}{\hbar^2} \left( E^* + \frac{E^{*2}}{E_G} \right) \right)^{\frac{1}{2}} \]  
\[ (15.21) \]

\[ \delta = \left( 2k_F r_{0,\infty} \right)^2 \]  
\[ (15.22) \]

\( \varepsilon_\infty \) is the high-frequency permittivity, where the unit is the permittivity of vacuum \( \varepsilon_0 \). Note that

the screening radius \( r_{0,\infty} \) is expressed in terms of the density of states \( g(E^*) \).

**Total Electron Relaxation Time**

The electron scattering rate is the reciprocal of the relaxation time. The total relaxation time can be calculated from individual relaxation time according to Matthiessen’s rule as

\[ \frac{1}{\tau} = \sum_i \frac{1}{\tau_i} \]  
\[ (15.23) \]

The Matthiessen’s rule assumes that the scattering mechanisms are independent of each other.

**15.5 Lattice Thermal Conductivity**

The detailed derivation for lattice thermal conductivity is found in Section 13.3. Here the expressions for low dimensions are added. From Equation (13.64), the *generic lattice thermal conductivity* is given by
\[ k_{\text{lat}} = C_{\text{branch}} \frac{k_B}{2\pi^2 v_s} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^\infty \tau_c \frac{x^4 e^x}{(e^x - 1)^2} dx \]  

(15.24)

\[ C_{\text{branch}} = 1 \text{ for bulk} \]  

(15.25)

\[ C_{\text{branch}} = \frac{2}{3} \text{ for 2D} \]  

(15.26)

\[ C_{\text{branch}} = \frac{1}{3} \text{ for 1D} \]  

(15.27)

where \( C_{\text{branch}} \) is the \textit{dimensionality factor of phonon branches} for low dimensions. There are mainly three acoustic branches (modes) in bulk Si, one longitudinal and two transverse. They each contribute about 1/3 of the thermal conductivity (The longitudinal optic contributes about 5\%, Esfarjani et al. (2011)[16].) In order to take account of the above low dimensional dimensionality factors, film thicknesses or nanowire diameters should be sufficiently small (an order of magnitude of nanometers). Otherwise, there will be an effect of 3D in the computed 1D results.

### 15.6 Phonon Relaxation Time

See Section 13.3.4 for phonon relaxation times. The phonon boundary scattering rate in Equation (13.78) is replaced for nanowires by[17]

\[ \tau_B^{-1} = \frac{v_s}{d} \left( \frac{1 - p}{1 + p} \right) \]  

(15.28)

where \( d \) is the nanowire diameter (originally known as Casimir length [17]), \( p \) is the specularity parameter (for specular, \( p = 1 \) and for diffuse, \( p = 0 \)).

### 15.7 Input Data for Bulk Si and Nanowires

Using the generic formulae developed above, we compute electronic and phonon transport properties for bulk Si and nanowires. The input data for the computations are listed in Table
15.1. Some available computations for Bismuth (Bi) nanowire are illustrated along with Si nanowires. The velocity of sound of $5.88 \times 10^5 \text{ cm/s}$ shown in Table 15.1 is calculated, which is comparable to the measurement of $6.4 \times 10^5 \text{ cm/s}$ by McSkimin (1953)[18]. There is always a discrepancy between model and measurements. Fine adjustments between them were made using the deformation potential $\Phi_a$, the vacancy charge $Z$ for electron scattering, and the Grüneisen parameter $\gamma$ for phonon scattering.

Table 15.1 Comparison between Bulk Si, Si nanowires and Bi Nanowires for Input Data used in Computations.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Bulk Si</th>
<th>Si Nanowires</th>
<th>Bi Nanowires$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{Si}$</td>
<td>Atomic mass (g)</td>
<td>28.086</td>
<td>28.086</td>
<td>208.98</td>
</tr>
<tr>
<td>$d_{Si}$</td>
<td>Mass density (g/cm$^3$)</td>
<td>2.33</td>
<td>2.33</td>
<td>9.80</td>
</tr>
<tr>
<td>$N_{\nu}$</td>
<td># of degeneracy (valleys)</td>
<td>6</td>
<td>6</td>
<td>2 - 3</td>
</tr>
<tr>
<td>$m_{de}^*$</td>
<td>Electron DOS effective mass ($m_0$)</td>
<td>0.409</td>
<td>0.409</td>
<td>~ 0.2</td>
</tr>
<tr>
<td>$m_{dh}^*$</td>
<td>Hole DOS effective mass ($m_0$)</td>
<td>0.245</td>
<td>0.245</td>
<td>~ 0.6</td>
</tr>
<tr>
<td>$E_G$</td>
<td>Bandgap (eV)</td>
<td>$1.17+1.059\times10^{-5}T$</td>
<td>$1.17+1.059\times10^{-5}T$</td>
<td>$0.038+2.1\times10^{-3}T + 2.5\times10^{-4}T^2$</td>
</tr>
<tr>
<td>$\theta_D$</td>
<td>Debye temperature (K)</td>
<td>645</td>
<td>645</td>
<td>112</td>
</tr>
<tr>
<td>$\Phi_a$</td>
<td>Deformation potential (eV)</td>
<td>5.5</td>
<td>5.5</td>
<td>-</td>
</tr>
<tr>
<td>$Z$</td>
<td>Vacancy charge in the unit of $e$</td>
<td>0.062</td>
<td>0.013</td>
<td>-</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Grüneisen parameter</td>
<td>0.53</td>
<td>0.53</td>
<td>-</td>
</tr>
</tbody>
</table>

Calculated from Input Data

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Bulk Si</th>
<th>Si Nanowires</th>
<th>Bi Nanowires$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_s$</td>
<td>Velocity of sound (cm/sec)</td>
<td>$5.88 \times 10^5$</td>
<td>$5.88 \times 10^5$</td>
<td>~ $2.5 \times 10^5$</td>
</tr>
<tr>
<td>$C_v$</td>
<td>Specific heat at 300 K (J/m$^3$K)</td>
<td>$1.66 \times 10^6$</td>
<td>$1.66 \times 10^6$</td>
<td>-</td>
</tr>
<tr>
<td>$n_{opt}$</td>
<td>Optimal electron concentration (cm$^{-3}$)</td>
<td>$\sim 1.8 \times 10^{19}$</td>
<td>$\sim 1.0 \times 10^{19}$</td>
<td>~ $10^{18}$</td>
</tr>
<tr>
<td>$d_{opt}$</td>
<td>Optimal nanowire diameter (nm)</td>
<td>-</td>
<td>~ 10</td>
<td>-</td>
</tr>
<tr>
<td>$ZT_{opt}$</td>
<td>Optimal or maximum $ZT$</td>
<td>~ 0.04</td>
<td>~ 2.7</td>
<td>~ 2.0</td>
</tr>
</tbody>
</table>

$^a$ Lin et al. (2000)
15.8 Bulk Si

Electronic transport properties for nanowires is based on the framework of bulk Si. Therefore, it is important that we have realistic electronic transport properties for bulk Si. It is reminded that the transport formulae in the previous sections are the same for bulk and nanowires except for the electronic density of states. In order to study the electronic performance for both bulk and nanowires, detailed results are presented. The following are the computed results.

Fermi Energy

The electron and hole (carrier) concentrations versus temperature are presented in Figure 15.1 (a), where we can see if the bipolar effect occurs. Bipolar effect is that pairs of carriers are generated due to elevated temperatures (where majority carriers move to the conduction band). A small bipolar effect is seen at 1000 K in the figure. The Fermi energy versus temperature along with the conduction and valence band edges is shown in Figure 15.1 (b). The Fermi energy is dependent on the doping concentration and temperature, when the bandgap is known. The position of the Fermi energy near the bandgap greatly affect the electron concentration. Note the variation of the valence band with increasing temperature, which is a typical phenomenon in thermoelectric materials, where the zero of the Fermi energy indicates the conduction band edge (minimum) in the present coordinate system. The variation of the Fermi energy against the doping concentration and temperature is shown in Figure 15.1 (c). Usually, the Fermi energy would lie close to the conduction band edge (zero) so that the Fermi-Dirac distribution causes the partial fill of electrons in the density of states (which would be required for a good Seebeck coefficient, not for electrical conductivity). The Fermi energy lies approximately at the zero where doping concentration reads about $1.8 \times 10^{19}$ cm$^{-3}$, which is the one used in the experimental values.
Figure 15.1 For n-type bulk Si, (a) carrier concentration versus temperature, (b) Fermi energy versus temperature, and (c) Fermi energy versus doping concentration.

**Electron Mobility**

Electron mobility is one of the most critical electronic properties of thermoelectric materials. Figure 15.2 (a) and (b) reveal that theoretical scattering mechanisms compare closely with measurements. Two mechanisms, acoustic phonons and ionized impurities, determine electron mobility and that the ionized impurity scattering rate is dominant at high electron concentrations.
Figure 15.2 For $n$-type bulk Si, (a) electron mobility at room temperature versus carrier concentration compared to experiments [19-22], (b) electron mobility versus temperature at carrier concentration of $1.8 \times 10^{19} \text{ cm}^{-3}$. The polar optical-phonon curve is not seen because it locates above the scale of mobility.

**Thermoelectric Transport Properties**

Electrical conductivity, Seebeck coefficient, and thermal conductivity for bulk Si are in general agreement with experimental values available for carrier concentration of $1.8 \times 10^{19} \text{ cm}^{-3}$ as shown in Figure 15.3(a), (b), and (c). Bipolar effect is seen at 900 K. The Seebeck coefficient appears sensitive to the bipolar effect. In Figure 15.3 (c), it is noted that the electronic contribution to the thermal conductivity is minimal.
Figure 15.3 For n-type bulk Si, (a) electrical conductivity, (b) Seebeck coefficient, and (c) total thermal conductivity with experiments [23, 24].

**Dimensionless Figure of Merit**

Figure 15.4 (a) and (b) show typical behaviors of transport properties against carrier concentration, leading to the optimal $ZT$ around carrier concentration of $1.8 \times 10^{19} \text{ cm}^{-3}$ as shown in Figure 15.4 (c). This optimal concentration approximately matches the concentration that has been used in the experimental data as shown in the figures. Note that the dimensionless figure of merit, $ZT = 0.04$
at the carrier concentration of about $1.8 \times 10^{19} \text{ cm}^{-3}$, is due to the high thermal conductivity of about 130 W/mK at 300 K.

Figure 15.4 For n-type bulk Si, (a) the Seebeck coefficient versus carrier concentration, (b) the electronic thermal conductivity and electrical conductivity versus carrier concentration, , and (c) the figure of merit versus carrier concentration.
15.9 Si Nanowires

15.9.1 Electron Properties

Fermi Energy and Carrier Concentration

Using the formulae in the previous sections, computations for nanowires were conducted with the input data in Table 15.1. The computed results for nanowires are presented in a similar way as were shown for bulk Si. Now we have a new parameter, the nanowire diameter $d$. We used Si nanowire diameter $d = 18$ nm and carrier concentration of $1.0 \times 10^{18}$ cm$^{-3}$ as a first attempt to compare carrier concentration and Fermi energy to bulk Si, which is shown in Figure 15.5 (a), (b), and (c). It is quite interesting that carrier concentrations and Fermi energy with a nanowire diameter of $d = 18$ nm are very similar to those in bulk Si. In Equation (15.2), we know that the density of states increases accordingly with decreasing the nanowire diameter. However, the electron concentration unexpectedly remains constant as the nanowire diameter decreases, which is shown in Figure 15.5 (d).
Figure 15.5 For n-type Si nanowires of $d = 18$ nm at carrier concentration of $1.0 \times 10^{18}$ cm$^{-3}$, (a) carrier concentration versus temperature, (b) Fermi energy versus temperature, (c) Fermi energy versus doping concentration, and (d) carrier concentration versus nanowire diameter.

**Electron Mobility**

Computed electron mobility for a nanowire with $d = 18$ nm is shown in Figure 15.6 (a) and (b). Although there is no experimental data for the nanowire to compare the computed mobility with, the ionized impurity scattering is the major mechanism at room temperature. At 500 K and above, all three mechanisms equally contribute to the mobility. This is somewhat different from that of bulk Si, where the ionised impurities predominate at all temperatures.
Figure 15.6 For $n$-type Si nanowires, (a) electron mobility at room temperature versus carrier concentration compared to bulk experiments [19-22], (b) electron mobility versus temperature at $d = 18$ nm and carrier concentration of $1.0 \times 10^{18}$ cm$^{-3}$.

**Thermoelectric Transport Properties for Si Nanowires**

It is seen from the experimental values in Figure 15.7 (a) and (b) that, as the measurement goes from bulk to nanowires, the electrical conductivity increases while the Seebeck coefficient decreases. It is supportive for the present model that both the computed curves approximately show the same trend. Slight bipolar effect in both computations occurs at 900 K.
Figure 15.7 For n-type Si nanowires at nanowire of 18 nm, (a) electrical conductivity versus temperature, and (b) Seebeck coefficient versus temperature. Experiments: Weber and Gmelin (1991)[24] and Hochbaum et al. (2008)[1]

Dimensionless Figure of Merit

Figure 15.8 (a) and (b) for a nanowire diameter of $d = 18$ nm shows a similar trend compared to those of bulk Si. Nevertheless, Figure 15.8 (c) shows that the optimal carrier concentration is shifted from about $1.8 \times 10^{19} \text{ cm}^{-3}$ in bulk Si to about $1 \times 10^{18} \text{ cm}^{-3}$ in nanowire. Figure 15.8 (d) shows the dimensionless figure of merit versus temperature, showing almost $ZT = 3$ at about 850 K. It is interesting to see that $ZT \approx 0.5$ at $1.8 \times 10^{19} \text{ cm}^{-3}$ in Figure 15.8 (c) is comparable to the value of $ZT = 0.6$ measured at $1.8 \times 10^{19} \text{ cm}^{-3}$ by Hochbaum et al. (2008)[1]. If this is applicable, the nanowire of Hochbaum would have a much higher $ZT$ value with doping (which requires an experimental proof). Figure 15.8 (c) shows good agreement with an ab initio simulation by Vo et al. (2008)[5].
Figure 15.8 For n-type Si nanowires, (a) Seebeck coefficient versus carrier concentration, (b) electronic thermal conductivity and electrical conductivity versus carrier concentration, (c) dimensionless figure of merit versus carrier concentration, and (d) dimensionless figure of merit versus temperature.

**Effect of Size for Nanowires**

In order to see only the electronic transport properties, not the phonon transport properties, with a variation of nanowire sizes, it is assumed that the lattice thermal conductivity has a constant value of 1 W/mK that is about the amorphous limit. (Hochbaum et al. (2008) [1] measured a thermal conductivity of ~ 1.6 W/mK with a nanowire of about 30 nm and Cahill et al. (1992)
measured the thermal conductivity of ~ 1 W/mK for amorphous silicon.) We believe that the amorphous limit of 1 W/mK can be achieved with nanowires in applications. We compare the present computed results with decreasing the size of nanowires to the work of Ramayya et al. (2012)[7], where they computed thermoelectric transport properties including the surface roughness of Si nanowires using Monte Carlo simulation. Figure 15.9 (a) and (b) shows the present Seebeck coefficient, electrical conductivity, and electronic thermal conductivity with decreasing the size of nanowires. The trends are in conceptual agreement with the work of Ramayya.

**Critical Nanowire Diameter**

In Figure 15.9 (c), as the nanowire diameter decreases, $ZT$ increases up to about 2.7 and decreases from a critical diameter of about 12 nm, which is also seen in the work of Ramayya. The cause of the critical diameter is conducted graphically to the electrical conductivity from Figure 15.9 (a) and (b) since both the Seebeck coefficient and the electronic thermal conductivity are in favor with $ZT$ as the nanowire diameter decreases. Since the electrical conductivity is proportional to the electron mobility, the electron mobility is plotted against nanowire diameter along with the scattering mechanisms. It is quite interesting to see that the dominance of scattering mechanisms is transformed near the critical diameter from ionized impurities to acoustic phonons with decreasing the diameter where the slope become steeper (Figure 15.9 (d)). This may be the cause of the critical nanowire diameter. The critical diameter of 12 nm is approximately comparable to the electron mean free path of 20 nm according to first-principles simulation by Qui et al. (2015)[26]. Having the nanowire diameter near the electron mean free path leads to additional boundary scattering, causing $ZT$ to drop. As a general strategy, the nanowires should be smaller than the phonon mean free path (about 300 nm) [27] but larger than the electron mean free path (about 20 nm) [26] so that phonons are more strongly scattered than electrons.
Figure 15.9 For $n$-type Si nanowires, (a) Seebeck coefficient versus nanowire diameter, (b) electronic thermal conductivity and electrical conductivity versus nanowire diameter, (c) dimensionless figure of merit versus nanowire diameter, and (d) electron mobility versus nanowire diameter, against nanowire diameters.

15.9.2 Phonon Properties for Si Nanowires

A great deal of research on phonon properties for nanowires has been reported with both measurements and computation (ab initio and Monte Carlo simulations). As a simple approach,
we use Equations (15.24) and (15.27) with a dimensionality factor of 1/3 for nanowires (see Section 15.5). Figure 15.10 (a) shows the computed results of lattice thermal conductivity for three nanowire diameters including bulk Si, along with measurements by Li et al. (2003) [28]. There is clearly an effect of this 1D model. Figure 15.10 (b) depicts the computed lattice thermal conductivity against nanowire diameters along with specularity parameters for \( p = 1, p = 0.8, \) and \( p = 0 \). This model indicates that to achieve lattice thermal conductivity of 1 W/mK requires a nanowire diameter of 1 nm with diffuse surfaces \( (p = 0) \). As mentioned earlier, this method is a simple approach with no effect of the rough surfaces of nanowires. Further studies are needed to explain the measured lattice thermal conductivity of 1.6 W/mK with a nanowire of about 30 nm by Hochbaum et al. (2008) [1], which is close to the amorphous limit.

Phonon scattering consists of the Umklapp (3-phonons), point-defect, electron-phonon, and boundary scattering mechanisms. Figure 15.10 (c) and (d) depicts the role of the individual weighted relaxation times for bulk Si and nanowires, respectively. The Umklapp scattering mainly appears dominant in bulk Si while the boundary scattering mainly appears dominant in Si nanowires, as expected.
Figure 15.10 For n-type Si nanowires, (a) lattice thermal conductivity versus temperature, (b) lattice thermal conductivity versus nanowire diameter, (c) weighted phonon relaxation time versus frequency for bulk Si, and (d) weighted phonon relaxation time versus frequency for Si nanowire. Experiments by Li et al. (2003) [28]

Problems

1. Derive in detail the generic electric conductivity of Equation (15.8).
2. Briefly, explain (200 words) why the critical nanowire diameter occurs based on the present model.
3. (Computer assignment) Develop a Mathcad program to provide the four plots of Figure 15.5 (a), (b), (c), and (d).
4. (Computer assignment) Develop a Mathcad program to provide the two plots of Figure 15.2 (a) and (b) including the experimental data (you need to do the curve fittings).
5. (Computer assignment) Develop/discuss a Mathcad model for lattice thermal conductivity for bulk Si and nanowires and provide two plots of Figure 15.10 (a) and (b) including the experimental data (you need to do the curve fitting). You may neglect the electron contribution to the thermal conductivity and may include your opinion in the discussion.
6. (Project) Develop/discuss a nonparabolic two-band model for generic thermoelectric transport properties for both bulk Si and nanowires, which includes electron scattering (using Mathcad). You may include your opinion in the discussion.

7. (Project) Develop/discuss a nonparabolic two-band model for generic thermoelectric transport properties for both bulk bismuth (Bi) and nanowires, which includes electron scattering (using Mathcad). You may include your opinion in the discussion.

8. (Project) Develop/discuss a nonparabolic two-band model for generic thermoelectric transport properties for graphene nanowires or nanotubes, which includes electron scattering (using Mathcad). You may include your opinion in the discussion.

References