Effect of growth base pressure on the thermoelectric properties of indium antimonide nanowires

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Abstract
We report a study of the effect of the growth base pressure on the thermoelectric (TE) properties of indium antimonide (InSb) nanowires (NWs) synthesized using a vapour–liquid–solid method at different base pressures varying from ambient to high vacuum. A suspended device was used to characterize the TE properties of the NWs, which are zinc-blende structure with \langle 110 \rangle growth direction based on transmission electron microscopy (TEM) characterization of the same NWs assembled on the suspended device. The obtained Seebeck coefficient is negative, with the magnitude being smaller than the literature bulk values and increasing with decreasing growth base pressure. These results are attributed to the loss of In from the source materials due to oxidation by residual oxygen in the growth environment and the consequent formation of Sb-doped NWs. The electron mobility and lattice thermal conductivity in the NWs are lower than the corresponding bulk values because of both surface scattering and stronger dopant scattering in the Sb-doped NWs. Based on these findings, it is suggested that growth from In-rich source materials can be used to achieve composition stoichiometry in the NWs so as to increase the Seebeck coefficient and TE figure of merit.

1. Introduction

Solid-state thermoelectric (TE) devices can be employed for direct thermal-to-electric energy conversion and refrigeration without emission of greenhouse gases [1]. The energy efficiency of TE devices depends on the dimensionless TE figure of merit (ZT), which is related to the electrical conductivity (\(\sigma\)), Seebeck coefficient (\(S\)) and thermal conductivity (\(\kappa\)) according to \(ZT = S^2\sigma T/\kappa\), where \(T\) is the absolute temperature. Recently, ZT values exceeding the long-held record of unity were demonstrated in nanostructured materials mainly because the lattice thermal conductivity is reduced by increased phonon-interface scattering [2, 3]. Power factor (\(S^2\sigma\)) increase and consequent ZT enhancement have also been reported in thallium doped PbTe, and attributed to an asymmetric local electron density of states (DOSs) caused by the thallium doping [4]. Well before ZT enhancement was demonstrated in these experimental investigations, theoretical calculations suggested that ZT enhancement can potentially be observed in bismuth-based and III–V nanowires (NWs) because of similar principles [5–8]. Besides the reduction in lattice thermal conductivity due to phonon scattering by the NW surface, the predicted ZT enhancement in these NWs was also attributed to quantum enhancement of the power factor because of an exceptionally asymmetric one-dimensional (1D) DOS in NWs resulting from the very small electron effective mass and long electron wavelength in Bi and some III–V compounds.

Among the III–V NWs examined in the reported TE transport calculations [7, 8], InSb NWs with the smallest
effective mass were predicted to possess the highest $ZT$, with calculated room-temperature values at the optimum carrier concentration much higher than unity when the NW diameter is smaller than 15 nm. In comparison, the reported peak $ZT$ value for bulk InSb has been 0.6 at 673 K [9]. In recent experimental investigations, Ye et al. [10] and Park et al [11] reported syntheses of single-crystal InSb NWs using the vapour–liquid–solid (VLS) process with indium and gold growth catalysts, respectively. Seol et al measured the electrical conductivity and Seebeck coefficient of some of Ye et al’s samples grown at ambient pressure using a nanofabricated device on an oxidized Si wafer [12, 13]. They found that the InSb NWs synthesized at ambient base pressure were n-type and highly degenerately doped, resulting in a low Seebeck coefficient.

The objective of this work is to investigate the effect of the base pressure during growth on the doping concentration and TE properties of InSb NWs. InSb NWs were synthesized at three different base pressures, namely ambient (760 Torr), low vacuum ($\sim 10^{-3}$ Torr) and high vacuum ($\sim 10^{-6}$ Torr). The thermal conductivity, Seebeck coefficient and electrical conductivity of NWs from these three different growth conditions were measured using a suspended microdevice [14–16]. The crystal structure and growth direction of the measured NWs were established using transmission electron microscopy (TEM). Transport models were used to analyse the measured TE properties in order to examine the influence of the growth base pressure on the doping concentration and to examine the effect of surface and dopant scatterings on the TE properties of the NWs. The measurement and analysis results suggest that the obtained NWs are more Sb-doped at a higher base pressure during the growth.

2. Experimental methods

2.1. NW synthesis

InSb NWs were grown using the VLS method in a tube furnace. High purity InSb powder (99.999% from Alfa Aesar) was loaded into a quartz boat that was placed into the middle part of a quartz tube as the source material. Pieces of Si wafers coated with a 300 nm thick thermally evaporated indium catalytic layer were loaded into the quartz tube and located downstream from the source. For growth under ambient base pressure, the tube furnace was first cleaned with argon gas for 30 min. Subsequently, the quartz tube was heated to 550°C to melt the source material with a flow of high purity hydrogen gas [17]. The temperature was maintained for typically 4–5 h. A representative scanning electron microscopy (SEM) image of the InSb NWs grown at ambient pressure appears in figure 1(a).

For growth under vacuum, the quartz tube was pumped for 1 h to a base pressure on the order of $10^{-3}$ Torr or $10^{-6}$ Torr, using a mechanical pump or a turbo pumping station, respectively. After the two ends of the quartz tube were sealed with vacuum valves, the furnace temperature was heated to 650°C to melt the source material and initiate the NW growth. The furnace temperature for vacuum growth was higher than that for ambient growth in order to compensate for the elimination of convective heat transfer from the heated quartz tube to the source material. In addition, the height of the vacuum-sealed tube was raised slightly to match the height of the pumping station. This resulted in poor thermal contact between the heater wires of the furnace and the quartz tube, thus necessitating a higher furnace temperature. At each base pressure under vacuum, the furnace temperature was kept at 650°C for 2–3 h. Subsequently, the heater was turned off and the temperature decreased to room temperature within 4–5 h.

Figure 1(b) shows a typical tilted SEM image of the as-grown InSb NWs under high vacuum. Although a few NWs were observed to be nearly vertical, most of the NWs appeared to be randomly oriented on the surface of the substrate. The x-ray diffraction (XRD) pattern from a 1 cm$^2$ wafer of NWs grown under high vacuum appears in figure 2. The three strongest peaks at 2θ $= 23.77°$, 39.31° and 46.46° identify the dominant phase as zinc-blende InSb (cubic, space group $F\bar{4}3m$, cell constant, $a = 6.478$ Å. JCPDS-PDF card number 00-006-0208 [18]). In this case, the peak intensity ratios differ slightly from those listed in the Powder Diffraction File (PDF) database; this is probably the result of some degree of preferential orientation among the NWs on the planar substrate [19, 20]. The In$_2$O$_3$ peaks denoted by * in figure 2 suggest the existence of the In$_2$O$_3$ phase in the sample, likely on the surface of the NWs.

2.2. NW characterization

The TE measurements were conducted using a suspended microdevice shown in figure 3, following procedures described in detail in previous publications [14, 16]. The device contained two silicon nitride ($\text{SiN}_x$) membranes, each suspended by six 400 µm long $\text{SiN}_x$ beams. One serpentine
Figure 2. XRD pattern of InSb NWs synthesized at high vacuum base pressure. The strong {hkl} peaks are from zinc-blende InSb. Reflections corresponding to In2O3 are indicated as ‘∗∗’.

Figure 3. SEM image of (a) the suspended device and (b) the two central membranes of the device showing InSb NW 3 trapped between the two membranes. Four small Pt patterns, labelled 1–4, were deposited on the NW using EBIMD in order to make electrical contact to the four pre-patterned Pt electrodes on the two membranes.

Pt resistance thermometer (PRT) covered by a silicon dioxide (SiO2) film and two additional Pt electrodes were patterned on each membrane. For each measurement, a NW was trapped between the two membranes and on top of the four exposed Pt electrodes. Because of the existence of a non-conducting oxide layer on the NW surface, the NW did not make electrical contact to the underlying Pt electrodes directly. Focused electron beam induced metal deposition (EBIMD) was used to deposit small Pt patterns, electrically connecting the NW to each underlying Pt electrode (labelled as 1, 2, 3 and 4 in figure 3(b)) in order to measure the four-probe electrical conductivity of the NW sample.

For the TE measurements, the suspended microdevice with an assembled NW was placed into the high vacuum sample space of a continuous flow liquid helium cryostat. The total thermal resistance ($R_t$) of each NW sample, including the contact thermal resistance, was obtained based on a two-probe thermal measurement [14], where the PRT on one membrane was heated electrically, and the temperatures on the two membranes were measured using the corresponding PRTs. A four-probe thermal measurement method [16] was used to obtain the contact temperature drops and contact thermal resistances for two of the NW samples (NW 2 and NW 3), enabling the intrinsic thermal resistance ($R_i$) and thermal conductivity of the NW sample to be obtained. The four-probe thermal measurement method relies on the measurement of the TE voltage ($V_{14}$) developed in the NW between the two outer contacts (1 and 4 in figure 3(b)) and that ($V_{23}$) between the two inner contacts (2 and 3 in figure 3(b)) when the PRT of one membrane was heated. The ratio $V_{23}/V_{14}$ was used to obtain the $R_i/R_t$ ratio and the intrinsic Seebeck coefficient of the NW based on a fit heat transfer model of the two NW segments in contact with the two membranes [16]. The intrinsic or four-probe Seebeck coefficient was found to be very close to the two-probe value measured using the two outer electrodes as $S_{14} = V_{14}/(T_h - T_s)$, because the temperatures at contact 1 and contact 4 were very close to $T_h$ and $T_s$, respectively, and the Seebeck coefficient of the Pt electrodes is much smaller than that of the NW.

The TE properties of four InSb NWs were measured in this work. Table 1 shows the diameter and the base pressure during growth for each of the four InSb NW samples as well as the InSb NW sample measured by Seol et al [13]. In Seol et al’s measurements, the NW was supported on a substrate with electrodes and resistance thermometers patterned on top of the NW sample. NW 1 and the sample measured by Seol et al were grown at ambient base pressure [10]. NW 2 was from low vacuum growth, while NW 3 and NW 4 were from high vacuum growth.

After the TE measurements, NW 2 and NW 4 were characterized using TEM, making use of a through-substrate hole in the suspended device. TEM was not performed on NW 1 and NW 3, because NW 1 was measured using a device from a previous design that did not have the through-substrate hole and NW 3 was broken during TEM sample preparation. Figure 4 shows the high-resolution TEM (HRTEM) image and selected area electron diffraction pattern of NW 2 after the TE measurement; the {220} fringes perpendicular to the NW axis indicate a ⟨110⟩ growth direction for this particular NW. It is also evident from figure 4 that there is a rough amorphous layer on the NW surface. The amorphous layer is mostly likely In2O3. NW 4 was also confirmed to have the zinc-blende structure with a ⟨110⟩ growth direction. These findings are consistent with the XRD results.
Table 1. The diameters, growth base pressures, extracted scattering parameters \( (r_e) \), carrier concentration \( (n) \), mobility \( (\mu) \) and neutral dopant concentration \( (N_n) \) of the InSb NWs. Also shown is the bulk mobility \( (\mu_{\text{bulk}}) \) at the given carrier concentration and \( \mu_{\text{ref}} \) calculated using the bulk impurity and phonon scattering rates and diffuse surface scattering \( (p_e = 0) \). Values outside (or inside) parentheses refer to the case that additional mobility reduction is caused by neutral impurity (or point defect) scattering. The extracted data for NW 4 are for a temperature of 350 K. The other data are for a temperature of 300 K. Vac = vacuum. N/A = not available.

<table>
<thead>
<tr>
<th>NW label</th>
<th>Diameter ( (\text{nm}) )</th>
<th>Base pressure</th>
<th>( r_e ) ( (\text{cm}^{-3}) )</th>
<th>( n ) ( (\text{cm}^{-3}) )</th>
<th>( N_n ) ( (\text{cm}^{-3}) )</th>
<th>( \mu ) ( (\text{cm}^2 \text{V}^{-1} \text{s}^{-1}) )</th>
<th>( \mu_{\text{bulk}} ) ( (\text{cm}^2 \text{V}^{-1} \text{s}^{-1}) )</th>
<th>( \mu_{\text{ref}} ) ( (\text{cm}^2 \text{V}^{-1} \text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seol</td>
<td>42</td>
<td>Ambient</td>
<td>$-0.161(-0.492)$</td>
<td>$8.1(5.4) \times 10^{18}$</td>
<td>N/A</td>
<td>$284(428)$</td>
<td>$9969(12663)$</td>
<td>$851(992)$</td>
</tr>
<tr>
<td>NW 1</td>
<td>133</td>
<td>Ambient</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>NW 2</td>
<td>144</td>
<td>Low Vac</td>
<td>$-0.035(-0.494)$</td>
<td>$6.4(3.8) \times 10^{18}$</td>
<td>N/A</td>
<td>$177(299)$</td>
<td>$11590(20716)$</td>
<td>$2301(3161)$</td>
</tr>
<tr>
<td>NW 3</td>
<td>177</td>
<td>High Vac</td>
<td>$-0.069(-0.479)$</td>
<td>$8.5(5.5) \times 10^{17}$</td>
<td>$2.2 \times 10^{16}$</td>
<td>$941(1449)$</td>
<td>$29861(33487)$</td>
<td>$5679(6484)$</td>
</tr>
<tr>
<td>NW 4</td>
<td>171</td>
<td>High Vac</td>
<td>$-0.131(-0.460)$</td>
<td>$5.9(4.2) \times 10^{17}$</td>
<td>$7.1 \times 10^{15}$</td>
<td>$1955(2764)$</td>
<td>$31873(38119)$</td>
<td>$6140(7058)$</td>
</tr>
</tbody>
</table>

Figure 4. HRTEM of InSb NW 2. The inset is the selected area electron diffraction pattern obtained using a beam size of 1.5 \( \mu \)m.

Figure 5. Seebeck coefficient \( (S) \) as a function of temperature \( (T) \) for five InSb NWs, bulk InSb reported by Yamaguchi et al and Bowers et al [9, 21].

3. Measurement results and discussion

3.1. Seebeck coefficient and electrical conductivity

Figure 5 shows the obtained Seebeck coefficients of four NWs measured in this work, together with measurement result by Seol et al [13] and data for bulk InSb reported by Yamaguchi et al [9] and Bowers et al [21]. The five InSb NWs all exhibit negative Seebeck coefficients, which indicate that the NWs were n-type. The absolute values of the Seebeck coefficient of the NWs are all smaller than the literature values shown in figure 5 for bulk InSb [9, 21] and increase with decreasing base pressure during the growth. For bulk InSb, the magnitude of Seebeck coefficient increases as temperature decreases from above 650 K to about 250 K. We note that this behaviour is not caused by the phonon-drag contribution, which is believed to be negligible in bulk InSb except for in the temperatures range between 10 K and 30 K [22]. In comparison, the measured Seebeck coefficient of the NWs, especially those grown at a higher base pressure, is more linear and metallic-like than the bulk data.

Figure 6 shows the electrical conductivity of the InSb NWs together with the bulk values reported in the literature [9, 21]. The electrical conductivity was not measured for NW 1 because the earlier batch of the measurement devices only had two contact electrodes and could not be used for four probe electrical measurements. Compared with the bulk electrical conductivity data that show an apparent thermal activation process, rather weak temperature dependences were observed in the measured electrical conductivity of the NWs. Hence, electron transport in the NWs appears to be in the extrinsic regime where the carrier concentration is not a strong function of temperature. The NW measured by Seol et al with the lowest Seebeck coefficient also shows the highest electrical conductivity among the four measured NWs. The NWs grown in vacuum with higher Seebeck coefficients have lower electrical conductivities than the NWs from ambient growth. This finding agrees with the general trend that the
Seebeck coefficient increases and the electrical conductivity decreases with decreasing carrier concentration. The lone exception is that NW 4 shows both a 20% higher Seebeck coefficient and 40% higher electrical conductivity than NW 3, even though both have similar diameters and were grown at the same high vacuum base pressure.

The measured $S$ and $\sigma$ results suggest that the electron concentration of the NWs increases with growth base pressure. A study of oxygen interaction with InSb surfaces suggested that the formation of $\text{In}_2\text{O}_3$ on the surface consumes In, resulting in Sb-rich, n-type InSb on the surface [23]. Although the surface oxide on the NW surface is likely $\text{In}_2\text{O}_3$ that results in n-type interface states, surface oxide alone is insufficient to explain the dependence of the electron concentration on the growth pressure, because the NW surface could be oxidized during exposure to air after growth so that similar surface oxide can be observed on NWs from different growth base pressures. On the other hand, residual oxygen in the NW growth environment can oxidize the source material to form $\text{In}_2\text{O}_3$ so that the growth environment is In-deficient and consequently the obtained NWs become Sb-doped and n-type. The oxidation rate increases with oxygen concentration in turn increases with the base pressure, so that NWs from ambient growth are more Sb-doped with higher electron concentrations than those from vacuum growth. On the other hand, even those samples grown at high vacuum base pressure appear to contain a high electron concentration. This result suggests that the NWs from high vacuum growth are still likely doped by excess Sb due to In oxidation by residual oxygen present in the tube furnace.

It has been reported that high mobility InSb thin films grown by metalorganic chemical vapour deposition (MOCVD) can be obtained only in In-rich environment [24], which might have helped to achieve composition stoichiometry. Besides providing preferred nucleation sites for the NW growth, the In catalyst layer on the growth substrate could possibly provide additional In vapour in the growth environment. However, the fact that high vacuum grown InSb NWs are still Sb-doped indicates that the In oxidation rate during the high vacuum growth is still too high to be compensated by the presence of the In catalyst layer on the growth substrate. Hence, in addition to minimizing residual oxygen in the growth environment, it would also be necessary to use In-rich source material to compensate the loss of In due to oxidation so as to achieve stoichiometry in the obtained NWs.

### 3.2. Electron concentration and mobility

We have determined the electron concentration and mobility from the measured Seebeck coefficient and electrical conductivity based on transport models. The small negative Seebeck coefficient values suggest that the measured InSb NWs were degenerately n-doped. Additionally, the ratio of electron mobility to hole mobility is approximately 100 for bulk n-type InSb [25]. Thus, the hole contributions to the transport coefficients should be negligible and are not included in the following analysis. First, the Seebeck coefficient of electrons in the conduction band is given by [26]

$$S = \frac{1}{eT} \left( E_F - \int_0^{\infty} g(E) \tau_0 E^2 e^{-\frac{\Delta f_0(E)}{\Delta E}} dE \right),$$

where $e$ is the elemental charge, $T$ is the absolute temperature, $g$ is the DOS for electrons, $\tau_0$ is the electron scattering mean free time and $f_0$ is the Fermi–Dirac distribution function that contains the Fermi level ($E_F$) measured from the conduction band edge. Because the diameter of each NW analysed here is much larger than the respective electron wavelength value between 11 and 30 nm calculated based on the Fermi level and the corresponding effective mass $m_e^*$, the bulk DOS has been used in the analysis. The electron energy ($E$) dependence of the relaxation time is assumed to take the form $\tau_e = \tau_0 E^{\gamma_e}$, where $\tau_0$ and $\gamma_e$ are constants. The value of $\gamma_e$ depends on the dominant scattering process. Both boundary scattering and acoustic phonon scattering yield a $\gamma_e$ value of $-0.5$ [15, 27].

For bulk InSb, it has been shown that optical phonon scattering with $\gamma_e \approx 0.5$ is the dominant scattering mechanism at temperatures near and above room temperature [28]. On the other hand, scattering of electrons by ionized impurities is ascribed an energy dependence with $\gamma_e$ between $-1/2$ and $3/2$ depending on the nature and strength of the impurity screening and the energy dependence of the DOS [29].

Using the measured room-temperature Seebeck coefficient data compiled by Rode [28] for n-type bulk InSb crystals at different carrier concentrations ($n$), we first determine the scattering parameter $r_{e,bulk}$ for bulk InSb at different $n$. At each given $n$ for the bulk crystal, the Fermi level is obtained from

$$n = \int_0^{\infty} g(E) f_0(E) dE.$$  

Here, the effective mass $m_e^*$ in the $g$ term depends on $n$ in InSb according to the literature [30]. The obtained $E_F$ at the $n$ value for the bulk crystals is further used together with the measured room-temperature $S$ at the same $n$ to determine the $r_{e,bulk}$ Value from equation (1). As shown in figure 7, the $r_{e,bulk}$ value for n-type bulk InSb crystals decreases from about 0.675 at $n = 5.0 \times 10^{16}$ cm$^{-3}$ to about $-0.225$ at $n = 1 \times 10^{19}$ cm$^{-3}$. We find that the as-extracted $r_{e,bulk}$ ($n$) values can be fitted by assigning a scattering parameter $r_{e,ph} = 0.8$ for phonon scattering and $r_{e,i} = -0.45$ for impurity scattering based on the following relation [31]

$$r_{e,bulk}(n) = \left[ \frac{r_{e,ph}}{\mu_{ph}} + \frac{r_{e,i}}{\mu_{i,bulk}(n)} \right] \mu_{bulk}(n),$$

where $\mu_{bulk}(n)$ is the mobility found in the literature for bulk InSb [28]. $\mu_{ph}$ is the phonon scattering mobility that is taken as the $\mu_{bulk}(n)$ value for the near intrinsic case at $n = 1.67 \times 10^{19}$ cm$^{-3}$ and $\mu_{i,bulk}(n)$ is the impurity scattering mobility obtained based on the Mathiessen’s rule, i.e.

$$\mu_{bulk}(n)^{-1} = \mu_{ph}^{-1} + \mu_i^{-1,bulk}(n)$$

We note that the obtained $r_{e,i} = -0.45$ value in doped bulk InSb crystals is close to the value of $-0.5$ for the strongly screened ionized impurity scattering case [29].
Because of the small band gap and typically very small activation energy of dopants in InSb, the majority of the excess Sb atoms are expected to be ionized in the measurement temperature range. Because of the electron concentration is high in the InSb NWs, we expect that impurity scattering by ionized Sb dopants remains strongly screened in the NWs with $r_{e,i} \approx -0.5$, which is the same as the value for boundary scattering and point defect scattering in the NWs [32]. On the other hand, the small fraction of the excess Sb atoms that are not yet ionized could lead to neutral impurity scattering with the scattering parameter $r_{e,n} = 0$ [29]. Hence, the $r_e$ value is expected to be in the range between $-0.5$ and 0 in the NWs given that the bulk value is already negative for electron concentration higher than $10^{18}$ cm$^{-3}$. Based on this analysis, we have used equation (1) to extract the $E_D$ from the measured $S$ of the NWs with $r_e$ in the range between $-0.5$ and 0.

For each $r_e$, the carrier mobility $\mu$ was determined using

$$\sigma = ne\mu,$$  \hspace{1cm} (5)

where $\sigma$ is the measured electrical conductivity of the NW and $n$ is the carrier concentration from equation (2). The as-obtained mobility $\mu$ is compared with $\mu_{ref}$, which is the NW mobility calculated for the case where only the boundary scattering rate is modified by surface scattering and other scattering rates are the same as those in bulk InSb at the same $n$. This value is obtained using Matthiessen’s rule

$$\mu^{-1}_{ref} = \mu^{-1}_{bulk}(n)^{-1} + \mu_{e,B}(n)^{-1},$$  \hspace{1cm} (6)

where $\mu_{e,B}$ is the boundary scattering mobility calculated by

$$\mu_{e,B} = \frac{eI_{e,B}}{m_e^{*2}v_e}.$$  \hspace{1cm} (7)

In equation (7), $v_e$ is the electron velocity that depends on $n$ and $I_{e,B}$ is the electron-boundary scattering mean free path that is evaluated according to

$$I_{e,B} = \frac{1 + p_e}{1 - p_e}d,$$  \hspace{1cm} (8)

where $d$ is the NW diameter and $p_e$ is the specularity parameter in the range between 0 and 1 and describes the probability of specular surface scattering of electrons [27].

For $r_e$ between $-0.5$ and 0, the obtained mobility was found to be much smaller than $\mu_{bulk}(n)$ and at least three times smaller than the $\mu_{ref}$ value obtained using $p_e = 0$ for completely diffuse surface scattering, as illustrated in table 1 where the $r_e$ value has been calculated for each NW based on the procedure discussed below.

The comparison between the obtained $\mu$ and $\mu_{ref}$ suggests that impurity scattering in the NWs is stronger than bulk crystals at the same carrier electron concentration. Bulk crystals reported in the literature were usually doped with substitutional tellurium (Te) at the Sb site to be n-type [33]. The Te donor atom has one extra valence electron compared with Sb with the valence difference $Z = 1$. In comparison, a substitutional Sb atom occupying the In site has two extra valence electrons with $Z = 2$. Ionized impurity scattering mobility ($\mu_{i}$) is proportional to $N_{i}^{-1}Z^{-2}$ [27], where $N_{i}$ is the concentration of the ionized impurities. For the same electron concentration $n \approx N_{i}Z$, $\mu_{i}$ is proportional to $Z^{-1}$ so that $\mu_{i}$ for Sb doping in the NWs is approximately half of the $\mu_{i,bulk}(n)$ value found from equation (4) for bulk crystals doped by Te to the same $n$. In addition, scattering by excess neutral Sb can give rise to additional mobility reduction. For this case,

$$\mu^{-1} = \mu_{ph}^{-1} + 2\mu_{i,bulk}(n)^{-1} + \mu_{e,B}(n)^{-1} + \mu_{e,n}^{-1},$$  \hspace{1cm} (9)

which can be used to obtain $\mu_{e,n}$, the mobility for additional neutral impurity scattering in the NWs. Because the NW surface appears to be rather rough, the $p_e$ in the $\mu_{e,B}$ term is assumed to be zero. The effective scattering parameter $r_e$ can further be obtained in an iterative procedure until equations (1), (2), (5) and (9) and the following relation are all satisfied

$$r_e(n) = \left[ \frac{r_{ph}}{\mu_{ph}} + \frac{2r_{e,i}}{\mu_{i,bulk}(n)} + \frac{r_{e,b}}{\mu_{e,B}} + \frac{r_{e,n}}{\mu_{e,n}} \right] \mu(n).$$  \hspace{1cm} (10)

However, the additional scattering may also be due to point defects for which $r_e = -0.5$ [32]. In this case, equation (9) needs to be modified as

$$\mu^{-1} = \mu_{ph}^{-1} + 2\mu_{i,bulk}(n)^{-1} + \mu_{e,B}(n)^{-1} + \mu_{e,PD}^{-1},$$  \hspace{1cm} (11)

which can be used to obtain $\mu_{e,PD}$, the mobility for additional point defect scattering in the NWs. Similarly, the effective scattering parameter $r_e$ can further be obtained in an iterative procedure until equations (1), (2), (5) and (11) and the following relation are all satisfied

$$r_e(n) = \left[ \frac{r_{ph}}{\mu_{ph}} + \frac{2r_{e,i}}{\mu_{i,bulk}(n)} + \frac{r_{e,b}}{\mu_{e,B}} + \frac{r_{e,PD}}{\mu_{e,PD}} \right] \mu(n).$$  \hspace{1cm} (12)

The obtained results are shown in table 1 for the case that additional mobility reduction is caused by either neutral impurity or point defect scattering, for the former of which the neutral impurity concentration ($N_a$) is determined to be...
The NW thermal conductivity was first calculated by assuming by fitting the MHS model to the thermal conductivity data. In that case, the suppressed mobility could be attributed to partially diffuse scattering of electrons by the NW surface. In comparison, NWs 2, 3 and 4 have much larger diameters than Seol et al.’s sample so that the effect of surface scattering is decreased and the effect of impurity scattering can be determined more readily. Even when the dependence of \( m^* \) on \( n \) is ignored, the obtained \( \mu \) values for NWs 2–4 are still lower than \( \mu_{\text{ref}} \). Hence, irrespective of the \( m^* \) data used in the analysis, diffuse surface scattering alone is insufficient to suppress the mobility to the experimental value for NWs 2, 3 and 4 of relatively large diameters. Therefore, impurity or defect scattering in these NWs is indeed stronger than the bulk value at the given carrier concentration because of the different ionized dopant types and the presence of a small fraction of neutral Sb dopants or point defects in the Sb-doped NWs. In addition, a higher concentration of neutral dopants or point defects in NW 3 than NW 4 with a similar diameter and from the same high vacuum growth could have caused the lower mobility and lower electrical conductivity despite a higher carrier concentration and lower Seebeck coefficient.

### 3.3. Thermal conductivity and figure of merit

In addition to Seebeck coefficient and electrical conductivity, the thermal conductivity was measured. Figure 8 shows the four-probe or intrinsic thermal conductivity of NW 2 and NW 3. Because of the contact thermal resistance, the four-probe thermal conductivity is higher than the two-probe thermal conductivity by about 15% for NW 2 and about 40% for NW 3. The intrinsic thermal conductivities of these two InSb NWs were found to be 3–4 times lower than the bulk values found in the literature [9, 35].

We note that the thermal conductivity of InSb is dominated by phonons at all but very high temperatures. In order to understand the thermal conductivity suppression in NWs, we have calculated the lattice thermal conductivity by using a modified Callaway model [36] reported by Morelli et al. [37], hereafter referred as the MHS model. The model adapted in this work consists of two adjustable parameters. One is the constant \( A \) in the frequency \( (\omega) \)-dependent impurity scattering rate \( \tau_{\text{i}}^{-1} = A\omega^s \), where \( A \) depends on the concentration of excess Sb atoms and point defects in the Sb-doped NWs. The second adjustable parameter is the boundary scattering mean free path, which is related to the surface specularity of the NW. For bulk InSb of \( 2 \times 10^{16} \text{ cm}^{-3} \) carrier concentration, the parameter \( A \) was obtained to be \( A_{\text{bulk}} = 1.7 \times 10^{-44} \text{ s}^3 \) by fitting the MHS model to the thermal conductivity data. The NW thermal conductivity was first calculated by assuming the same amount of impurity level with bulk by using the same A value. Because the TEM analysis reveals a ~3 nm surface roughness, which is larger than the dominant phonon wavelength (\( \lambda \)) on the order of 1 nm in the temperature range, phonon scattering by the NW surface was taken as diffuse based on Ziman’s expression for surface specularity [27]. Consequently, the boundary scattering mean free path is taken as the NW diameter \( d \). As shown in figure 8, the calculation results using the \( A_{\text{bulk}} \) value are higher than the measurement values of the two NWs. The calculation can match the measurements when the \( A \) value is increased to \( 2.35 \times 10^{-43} \text{ s}^3 \) for NW 2 and \( 1.55 \times 10^{-43} \text{ s}^3 \) for NW 3. By comparing the calculation results based on the two different \( A \) values for each NW, moreover, we determine that approximately about 2/3 of the thermal conductivity reduction near room temperature is due to diffuse phonon-surface scattering and remaining 1/3 is due to increased impurity scattering in the NWs. In addition, the \( A \) value used to fit the NW 2 data is about 50% higher than that used to fit the NW 3 data, in agreement with the finding based on the measured \( S \) and \( \sigma \) that NW 2 grown from low vacuum base pressure has more excess Sb dopants or point defects than NW 3 grown at high vacuum base pressure.

The \( ZT \) values of the NWs are obtained from the measured four-probe thermal conductivity, Seebeck coefficient and electrical conductivity as shown in figure 9. Despite the reduced lattice thermal conductivity, the \( ZT \) of the two NWs is about 10 times lower than the bulk values because of the lower Seebeck coefficient in NWs than the bulk. In addition, NW 3 from the high vacuum growth shows higher \( ZT \) values than the low vacuum grown NW 2.
4. Conclusion

InSb NWs have been synthesized at three different base pressures varying from ambient pressure to $10^{-6}$ Torr in order to investigate the effects of growth base pressure on the doping and transport properties of these NWs. The TE properties of the NWs were characterized using a suspended device that allows TEM characterization of the NWs. The measured NWs were found to be zinc-blende structure with $\langle 110 \rangle$ growth direction. XRD and TEM results suggest the formation of In$_2$O$_3$ on the NW surface. The Seebeck coefficient was found to be negative, suggesting that the NWs were doped to be n-type. The magnitude of the Seebeck coefficient of the NWs is lower than the reported bulk values and increases with decreasing base pressure. These results are attributed to the preferential oxidation of In in the source material to form Sb-rich growth environment and thus Sb-doped n-type NWs. The NWs from ambient growth are more Sb-doped than those from vacuum growth because of a higher oxygen concentration. The electron mobility in the Sb-doped NWs is lower than that of bulk crystals doped with Te to the same carrier concentration because of both diffuse surface scattering and stronger ionized and neutral dopant or point defect scattering. Similarly, the lattice thermal conductivity of the NWs was found to be suppressed by diffuse phonon-surface scattering and higher phonon-dopant or point defect scattering rates than those in bulk crystals reported in the literature. Moreover, a higher phonon-dopant or defect scattering rate was found in a NW from low vacuum growth than the other from high vacuum growth. Despite the large thermal conductivity suppression, the $ZT$ of the two NWs is about 10 times lower than the reported bulk values because of the suppressed Seebeck coefficient and reduced mobility in the NWs. One NW from the high vacuum growth shows higher $ZT$ values than another low vacuum grown NW. These results suggest the need of new approaches to better controlling the impurity doping and surface scattering in order to optimize the carrier concentration and improve the mobility. One of such approaches is to use In-rich source materials to compensate the loss of In due to oxidation so as to achieve composition stoichiometry in the NWs.

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