Diameter dependence of the thermal conductivity of InAs nanowires

van Delft, M.R.

Award date:
2014

Link to publication
Diameter dependence of the thermal conductivity of InAs nanowires

M.R. van Delft
m.r.v.delft@student.tue.nl

August 4, 2014
Abstract

A systematic experimental investigation was performed of the thermal conductivity of InAs wires with diameters between 40 and 1500 nm. The thermal conductivity has been shown to vary significantly between a large number of similar nanowires smaller than 250 nm. Any dependence on the diameter was obscured by this variation. On average, the thermal conductivity was $3.9 \pm 1.0 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$, which is a considerable reduction from bulk and shows that surface scattering is important. This value is in agreement with other measurements and theory.

For wire diameters larger than 700 nm, an extremely low apparent conductivity was measured. For these wires, values near the bulk level of $27 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$ were expected, but values smaller than for the thin wires were obtained instead. This is a consequence of contact resistance. The contact conductance is proportional to the contact area and thus to the diameter of the wire. The conductance of the wire itself on the other hand, is proportional to the diameter squared. This means that for increasingly thick wires, the conductance of the wire becomes much larger than that of the contacts, and the overall measured conductivity becomes dominated by the contacts. This trend was reproduced in a simple qualitative model.
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>Electrical measurements</td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td>Conclusions and outlook</td>
<td>56</td>
</tr>
<tr>
<td>6.1</td>
<td>Conclusions</td>
<td>56</td>
</tr>
<tr>
<td>6.2</td>
<td>Outlook</td>
<td>56</td>
</tr>
<tr>
<td>7</td>
<td>Acknowledgements</td>
<td>57</td>
</tr>
<tr>
<td>A</td>
<td>Properties of different nanowire growths</td>
<td>61</td>
</tr>
<tr>
<td>B</td>
<td>Properties of used materials</td>
<td>62</td>
</tr>
<tr>
<td>B.1</td>
<td>Indium arsenide</td>
<td>62</td>
</tr>
<tr>
<td>B.2</td>
<td>Silicon nitride</td>
<td>62</td>
</tr>
<tr>
<td>B.3</td>
<td>Platinum</td>
<td>62</td>
</tr>
<tr>
<td>C</td>
<td>Equations</td>
<td>63</td>
</tr>
<tr>
<td>C.1</td>
<td>Device asymmetry</td>
<td>63</td>
</tr>
<tr>
<td>C.2</td>
<td>Radiation view factor</td>
<td>63</td>
</tr>
</tbody>
</table>
1 Introduction

There has been considerable interest in the development of thermoelectric materials for about 100 years now. These materials allow for the conversion of a temperature difference to a voltage, or the conversion of a voltage to a temperature difference: the Seebeck and Peltier effects, respectively. The potential applications of these materials are many and include the ability to generate electricity from waste heat or make more environmentally friendly refrigerators. There is a problem however, as the efficiency is still very low. Thermoelectric research is therefore focussed on increasing the efficiency.

Now, thermoelectric materials may still have limited efficiency, but they do have advantages that cause them to be used in certain niche applications. A large advantage for example, is the lack of any moving parts. Because of this, thermoelectric modules require very little maintenance and can continue to work unattended for many years. This is particularly convenient for use in locations which are difficult to reach, such as outer space, where thermoelectric power generators are used to convert heat from nuclear fissile material to electricity in order to power spacecraft where sunlight is not strong enough. Other advantages of thermoelectric systems are that they can be made very small, have a rapid response time and require no environmentally unfriendly refrigerants to perform cooling.

It will however take a significant improvement of the materials used in thermoelectrics before these advantages will outweigh the disadvantages for common applications. If that can be achieved, the impact to society will be significant. As efficient thermoelectric cooling systems replace conventional systems, the powerful greenhouse gases used as refrigerants today will no longer be needed, benefitting the environment. Using thermoelectrics, microprocessors could be cooled locally at hot-spots and as the performance of these processors often decreases rapidly with increased temperature, this is very beneficial. Thermoelectrics can also provide great benefits when used for power generation. In this case, for example, it could be used to convert waste heat from car engines or industrial processes directly into electricity without consuming additional fuel.

The first thermoelectric materials that were used in niche applications were developed in the 1950s. These were Bi$_2$Te$_3$ and various alloys with Sb or Se. After the discovery of these materials, it took until the turn of the millennium for significant improvements to be made. This is related to the development of fabrication techniques for nanostructured materials, which can exhibit an increased efficiency. Superlattices of thin films for example have led to improvements [1].

Another proposed system for a thermoelectric material is the nanowire. Nanowires are predicted to show a large boundary scattering of phonons. For thinner nanowires, the boundary plays in increasing role in the system and scattering is further enhanced. This is a very beneficial property for thermoelectrics that can significantly increase the efficiency. An even greater enhancement is expected when a wire is thin enough to show the characteristic onedimensional density of states, as this DOS can increase the strength of the thermopower [2].

The aim of this work is to investigate the use of nanowires as a thermoelectric material. To this end, the thermal conductivity of nanowires is measured over a large range of nanowire diameters. The thermal conductivity is an important parameter for a thermoelectric material, and should be as low as possible.

The wires that are used in this project are made of indium arsenide (InAs). It is not expected that InAs itself will be useful as a thermoelectric material, even with very thin nanowires, but it is relatively simple to work with and can serve as a model system for different materials. Several others have measured the thermal conductivity of InAs nanowires [3],[7], but there has been no comprehensive study of the effects of different diameters.

The theoretical background of thermoelectrics and thermal conductivity is explained in Sec. 2 and the properties of nanowires in general and those of this work in particular are discussed in Sec. 3. A description of the measurement methods and devices is given in Sec. 4 and finally the results are discussed in Sec. 5.
2 Theory

The aim of this section is to explain in some detail what thermoelectrics really is, what it is good for and what are the important parameters (Sec. 2.1 and 2.2). The thermal conductivity is central to this work and is therefore discussed more rigorously. An expression for it is derived in Sec. 2.3 and the different scattering mechanisms that can serve to reduce it are described in Sec. 2.4. An explanation of thermal contact resistance is given in Sec. 2.5 and finally the electrical conductivity is briefly described in Sec. 2.6.

2.1 Thermoelectrics

A number of effects are included within thermoelectrics. The most important ones are the Seebeck effect, which causes an electromotive force to be produced as a result of a temperature difference, and the Peltier effect, which produces heating or cooling as an electric current is passed through a thermocouple. A third effect, the Thomson effect, causes heating or cooling under the influence of both an electric current and a temperature gradient. Additionally, there are some effects that occur only in a magnetic field: the thermomagnetic Nernst and Ettingshausen effects.

2.1.1 Seebeck effect

The Seebeck effect was discovered in 1821 by T. J. Seebeck, who showed that an electromotive force could be produced by heating the junction between two different materials. He initially included magnetism in his explanation of this effect, but this was later proven incorrect by Lord Kelvin, who also showed that the Seebeck coefficient is a measure of the entropy associated with electric current [8].

Consider a system with two different conductors, \(A\) and \(B\). \(A\) is connected to \(B\) at both ends, while \(B\) is divided in two parts between which a voltage meter can be placed, see Fig. 1.

![Figure 1: A simple thermocouple.](image)

A temperature difference \(\Delta T\) is then applied between the two junctions, while the two ends of \(B\) are kept at the same temperature. In general, this will cause a potential difference \(V\) to appear between the two ends of \(B\). The differential Seebeck coefficient is then:

\[
S_{AB} = \frac{V}{\Delta T}.
\]

(1)

\(S_{AB}\) is considered positive when the electromotive force tends to drive a current from hot to the cold junction, and negative otherwise [9].

It is also possible to define an absolute Seebeck coefficient, \(S\), for a specific material, rather than the differential coefficient considered so far. This can be done by taking the Seebeck coefficient of one of the two materials to be zero. In practice, that could be realized by using a superconductor as the second material, as superconductors have a Seebeck coefficient of zero.
To understand what determines the Seebeck coefficient in a material, it is important to understand how the Seebeck effect works at a fundamental level. As one side of a material is heated, that means that more charge carriers occupy high energy levels on that side. These high-energy charge carriers then diffuse towards the cold side. Simultaneously, low-energy carriers diffuse from the cold to the hot side. The magnitude of the Seebeck coefficient then depends on the difference in conductivity between the high- and low-energy charge carriers while the sign also depends on the type of carriers that is dominant, electrons or holes. As a result, the Seebeck coefficient is positive in p-doped and negative in n-doped semiconductors.

An expression for the Seebeck coefficient can be derived from Boltzmann transport theory based on this principle. This gives Mott’s formula:

\[ S = \frac{\pi^2 k_B^2 T}{3e} \left( \frac{d \ln N(E)}{dE} \right)_{E=E_F}, \]

with \( N(E) \) the density of states. This formula is particularly useful to see what affects the Seebeck coefficient. It is expected to increase with temperature, and is strongly affected by the density of states at the Fermi level. This dependence is something that can be used to increase the Seebeck coefficient.

### 2.1.2 Peltier effect

The Peltier effect was discovered 13 years after the Seebeck effect, by J. Peltier. Here, an electric current that is passed through a junction causes heating on one side and cooling on the other side of that junction, depending on the direction of the current.

Consider the same geometry as before, shown in Fig. except this time with a voltage source connected between the two parts of \( B \). Applying a voltage then causes a current, \( I \), to flow through the circuit while heating one junction and cooling the other. With the rate of heating or cooling being \( Q \), the differential Peltier coefficient is defined as:

\[ \Pi_{AB} = \frac{Q}{T}. \]

The Peltier coefficient is considered positive if the junction where it enters \( A \) is heated and the other junction is cooled. It can also be expressed in terms of the Seebeck coefficient through the Kelvin relation:

\[ \Pi_{AB} = S_{AB} T. \]

An absolute Peltier coefficient, \( \Pi \), can be defined in the same way as the absolute Seebeck coefficient.

### 2.1.3 Thomson effect

The Thomson effect was the last of the thermoelectric effects to be discovered, in 1851 by W. Thomson (who later became Lord Kelvin). Thomson recognized the relation between the Seebeck and Peltier effects and showed that there must be a third thermoelectric effect, which he was able to observe experimentally. This effect consists of heating or cooling of a material under the influence of both an electric current and a temperature gradient. The Thomson coefficient, \( \tau \), can be derived from the Seebeck coefficient:

\[ \tau = T \frac{dS}{dT}. \]

### 2.1.4 Thermoelectric devices

Basic designs for thermoelectric devices that utilize the Seebeck or Peltier effects are shown in Fig. These devices consist of two legs of n-doped and p-doped semiconductor material, connected by an electrical conductor to form a circuit. Because of the difference in doping, the dominant charge carriers, electrons or holes, in either side of these devices have opposite charge. This means that the carriers will move and transport heat in the same direction while a current passes through the device.
To make an effective thermoelectric cooling/heating module or a power generator, a large number of these devices is usually connected electrically in series and thermally in parallel.

The potential applications of these devices are manifold, yet very few have actually seen use in commercial applications so far. The main reason for this is the low efficiency of thermoelectric devices. In order to be competitive with other technologies, the efficiency needs to increase and/or the cost needs to decrease. And although there are some advantages which can be gained by optimizing the design and fabrication of the devices, the greatest performance increase can be achieved by improving the quality of the thermoelectric materials used.\[13\]
2.2 Thermoelectric figure of merit

The efficiency of a thermoelectric material is a function of the dimensionless thermoelectric figure of merit, which is defined as:

\[ ZT = \frac{S^2\sigma T}{\kappa}, \]  

with \( S \) the Seebeck coefficient, \( \sigma \) the electrical conductivity, \( \kappa \) the thermal conductivity and \( T \) the absolute temperature. In order for a thermoelectric material to be competitive with energy conversion technologies that are already commonly used, \( ZT \) has to be larger than 3 \([14]\).

A \( ZT \) of 3 is unfortunately not easily achievable. This has to do with the fact that all the parameters that determine \( ZT \) are related, such that for example an increase of \( \sigma \) will also lead to an increase of \( \kappa \) and vice versa. This is also illustrated in Fig. 3 which shows how semiconductors are better than insulators or metals for thermoelectrics. It is good to note that \( \kappa \) can be split into two contributions, one from electrons, \( \kappa_e \), and one from phonons, \( \kappa_l \). The latter contribution dominates in semiconductors, and is of particular interest because it can be controlled independently. In bulk semiconductors, \( \kappa_l \) can be reduced by using semiconductors of high atomic mass, such as Bi\(_2\)Te\(_3\) \([1]\). A higher atomic mass reduces the speed of sound in a material, and thus the phononic part of the thermal conductivity, without reducing the other parameters.

![Figure 3: A) The interdependency of S and \( \sigma \), as function of carrier concentration. B) Contributions to the thermal conductivity from electrons and the lattice, for insulators, semiconductors and metals. Figure adapted from [15].](image)

Bi\(_2\)Te\(_3\) was the first thermoelectric material with a high enough \( ZT \), about 0.6, to be usable in certain niche applications. It was discovered in the 1950s and for nearly 50 years after this discovery, very little progress was made and no materials could be produced with a \( ZT \) of more than 1. This only changed after the year 2000, when new techniques to fabricate nanostructured materials were used. The use of thin films of semiconductor material in heterostructures, for example, proved to be effective and lead to a record-high \( ZT \) of 2.4 at 300 K \([16]\) in 2001 and 2.6 at 923 K \([17]\) in 2014.

Another promising approach to increase \( ZT \) is to use onedimensional materials, i.e. nanowires. This was first suggested by Hicks and Dresselhaus \([2]\) in 1993. There have been several attempts to demonstrate this since then, but large enhancement of \( ZT \) due to the predicted 1D effects has not been clearly shown. There have been improvements to \( ZT \) made with nanowires, but those are related to an increase in surface scattering because of the high surface to volume ratio. Promising results were achieved for
example with silicon \[18\][19], reaching \(ZT \approx 1\). The advantages of nanowires will be discussed in more detail later on.

### 2.2.1 Thermoelectric efficiency

As mentioned before, the efficiency of thermoelectric devices depends on the \(ZT\) of the materials that are used. But \(ZT\) is not the only parameter determining the efficiency. The temperatures on the hot and cold sides of the device are important factors as well, both because the efficiency directly depends on these temperatures and because \(ZT\) is temperature dependent. Additionally, the actual performance of a device is also determined by the load resistance. Assuming that the temperature difference is such that \(S, \sigma\) and \(\kappa\) do not change, it can be derived that the efficiency, \(\eta\), at which thermal power is converted to electrical power is:

\[
\eta = \eta_c \frac{m/(m+1)}{1 + \frac{m+1}{Z_{12}} T_H/(m+1)} ,
\]

with \(m\) the ratio between the load resistance \(R\) and the sum of the resistances of the two legs of the device \[20\]. \(\eta_c\) is the Carnot efficiency, which is the fundamental limit for the efficiency, and \(Z_{12}\) is defined for the two different materials, or the n- and p-doped sections of the same material, that are used in the device:

\[
Z_{12} = \frac{S_2^2}{\sqrt{\kappa_1 \rho_1} + \sqrt{\kappa_2 \rho_2}}
\]

where \(\kappa_{1,2}\) and \(\rho_{1,2}\) are the thermal conductivity and electrical resistivity of both materials.

The actual efficiency of a device follows when a value for \(m\) is chosen. There are primarily two options in the choice of \(m\) for optimization of the device. The resistances can be optimized to generate maximum power. This requires that the load resistance is equal to that of the device, so that \(m=1\). Under those circumstances, the efficiency can never be higher than \(\frac{2}{3} \eta_c\).

The device can also be optimized for maximum efficiency, with \(\partial \eta / \partial m = 0\), so that

\[
m = \sqrt{1 + Z_{12} \bar{T}},
\]

with \(\bar{T}\) the average temperature. It then follows that

\[
\eta = \eta_c \frac{\sqrt{1 + Z_{12} \bar{T}} - 1}{\sqrt{1 + Z_{12} \bar{T}} + T_c/T_H},
\]

with

\[
\eta_c = \frac{T_H - T_c}{T_H}.
\]

For a cooling device, the equation is different and also the Carnot efficiency is defined differently \[14\]:

\[
\eta = \eta_c \frac{\sqrt{1 + Z_{12} \bar{T}} - T_H/T_c}{\sqrt{1 + Z_{12} \bar{T}} + 1},
\]

with

\[
\eta_c = \frac{T_c}{T_h - T_c}.
\]

In reality, the load resistance can not simply be chosen to optimize the device, meaning the efficiency will not be as high as these equations suggest. Regardless, it does still increase with increasing \(ZT\), making a higher \(ZT\) the goal of most research on thermoelectrics.
2.3 Thermal conductivity

The flow of heat through a material, or the thermal conductance of the material, obeys Fourier’s law:

\[
\vec{Q} = -\kappa \vec{\nabla} T,
\]

(14)

with \(\vec{Q}\) the heat flux in W·m\(^{-2}\), \(\kappa\) the thermal conductivity in W·m\(^{-1}\)K\(^{-1}\) and \(T\) the temperature in K. The thermal conductivity depends on the material and geometry of the system, and should be as small as possible in order to achieve a high \(ZT\).

Using simple kinetic theory, it is possible to derive an expression for the thermal conductivity in terms of other system parameters. Consider first the rate of change of the energy of a particle with velocity \(\vec{v}\) under a thermal gradient \(\vec{\nabla} T\):

\[
\frac{\partial E}{\partial T} = c\vec{v} \cdot \vec{\nabla} T,
\]

(15)

with \(c\) the heat capacity of a single particle. The particle travels an average distance \(\lambda = v\tau\), with \(\tau\) the relaxation time, before being scattered. This \(\lambda\) is called the mean free path. Summing over all particles, with concentration \(n\), then gives the total heat flux:

\[
\vec{Q} = -nc\tau \langle \vec{v} \cdot \vec{v} \rangle \vec{\nabla} T = -\frac{1}{3} nc\tau v^2 \vec{\nabla} T,
\]

(16)

where the brackets represent an average over all particles. Combining Eqs. 14 and 16 gives:

\[
\kappa = \frac{1}{3} nc\tau v^2 = \frac{1}{3} C v \lambda,
\]

(17)

with \(C = nc\) the total heat capacity. The same derivation can be made for various kinds of particles, so that the total thermal conductivity becomes:

\[
\kappa = \frac{1}{3} \sum_\alpha C_\alpha v_\alpha \lambda_\alpha,
\]

(18)

where the sum is over all different types of particles. In practice, the thermal conductivity can not be calculated exactly [21].

For the most part, heat conduction in solids takes place through electrons and phonons. That means that the total \(\kappa\) consists of two contributions, one electronic and one lattice contribution, such that:

\[
\kappa = \kappa_e + \kappa_l.
\]

(19)

In semiconductors, the lattice contribution, \(\kappa_l\), is typically much larger than the electronic contribution, \(\kappa_e\) [14]. Additionally, \(\kappa_e\) is directly related to the electrical conductivity via the Wiedemann-Franz law:

\[
\frac{\kappa_e}{\sigma} = LT,
\]

(20)

with \(L = (\pi^2/3)(k_b/e)^2\), the Lorenz number. This means that a decrease of \(\kappa_e\) leads to a decrease of \(\sigma\) and vice versa, making this ineffective as a way to increase \(ZT\). \(\kappa_l\) is also connected to the other parameters that determine \(ZT\), as all of these depend on the material, but it can be controlled independently, for example through nanostructuring of a material. For these reasons, the lattice contribution is of more interest than the electronic one for increasing \(ZT\) in semiconductor materials.
2.4 Phonon scattering

In a crystal, the lattice contribution arises from heat conduction through vibrational modes of the lattice, i.e. phonons. Two different types of phonons exist, the low-frequency acoustic modes and the high-frequency optical modes. Optical modes do not directly contribute to the conduction of heat because of their small group velocity. However, they can still interact with the acoustic phonons and thereby influence the thermal conductivity.

There are several scattering mechanisms that limit phonon heat conduction. In a pure bulk crystal at high temperature, phonons are scattered predominantly by other phonons in processes involving three phonons. These can be either normal scattering, where energy and momentum are conserved, or Umklapp scattering, where momentum is not conserved. The normal processes do lead to a redistribution of phonons, but not to thermal resistance, while the Umklapp processes control the thermal conductivity [8].

In a normal process, two phonons with wave vectors $q_1$ and $q_2$ interact and form a third phonon with $q_3$, such that

$$q_1 + q_2 = q_3.$$  \hfill (21)

In an Umklapp process, the sum of $q_1$ and $q_2$ lies outside the Brillouin zone. Therefore, the reciprocal lattice vector $G$ is subtracted to produce a $q_3$ that is allowed. The rule for the conservation of the wave vector for Umklapp scattering then becomes:

$$q_1 + q_2 = q_3 + G.$$  \hfill (22)

Phonons can also be scattered by defects, such as impurities or vacancies in the lattice. These defects produce local variations in density or elastic constants, causing a change in the speed of sound. The relaxation time for these processes varies as $\omega^{-4}$, with $\omega$ the frequency of the phonons. Because of this, the low-frequency phonons are not strongly scattered by impurities.

As the relaxation time for Umklapp scattering is proportional to $\omega^{-2}$, those processes also do not strongly scatter low-frequency phonons. Considering this, one might expect the low-frequency phonons to lead to a large thermal conductivity, as neither impurities nor Umklapp processes affect them significantly. This does not happen however, as normal processes redistribute these phonons into higher frequency modes that are more strongly scattered [8].

The effect of the normal processes can be taken into account with a method developed by Callaway [22]. In effect, this method requires the relaxation time for the processes that do not conserve momentum, $\tau_r$, to be replaced with a relaxation time that also depends on that of the normal processes, $\tau_N$:

$$\frac{1}{\tau_{\text{eff}}} = \left( \frac{1}{\tau_r} + \frac{1}{\tau_N} \right) \left( 1 + \frac{\beta}{\tau_N} \right)^{-1},$$  \hfill (23)

where $\beta$ is a constant that is selected so that the normal processes do indeed conserve momentum.

When there are multiple sources of scattering present, as is usually the case, that can be taken into account using Matthiessen’s rule:

$$\frac{1}{\tau_{\text{total}}} = \sum_i \frac{1}{\tau_i},$$  \hfill (24)

for different sources of scattering $i$.

2.4.1 Boundary scattering

Another mechanism that may reduce the thermal conductivity from phonons is boundary scattering, occurring at the edges of a single crystal or at grain boundaries in a polycrystalline sample. This mechanism is especially important at low temperature, where long-wavelength acoustic phonons are the dominant heat carriers. This regime where boundary scattering is important was already analysed in 1938 by Casimir [23], who found that the mean free path of the phonons becomes comparable to the system dimensions at sufficiently low temperature. For a cylindrical system, this means the mean
free path becomes equal to the diameter, $D$, assuming that the scattering at the surface is perfectly diffusive \cite{24}. The relaxation time then becomes:

$$\tau_b = \frac{D}{v},$$

with $v$ the phonon velocity. The assumption of perfectly diffusive scattering is not necessarily correct as the scattering may also be partially specular. For more specular scattering, the relaxation time becomes larger and $\kappa$ will be decreased less. For perfectly specular scattering, which also requires a perfectly smooth surface, $\tau_b$ even becomes infinite.

Boundary scattering is certainly not exclusively a low-temperature effect however. Low-frequency, long-wavelength phonons may not be as numerous at higher temperatures, but they do have a significant effect on the thermal conductivity as the higher-frequency phonons are more strongly scattered by Umklapp or impurity scattering. Scattering of long-wavelength phonons by crystal boundaries can therefore still reduce the thermal conductivity. This is illustrated in Fig. 4.

![Figure 4: Contribution to the lattice thermal conductivity by phonons of frequency $\omega$. The upper curve represents the situation where only phonon-phonon scattering occurs. The black region is that which is removed by impurity scattering and the grey region is removed by boundary scattering \cite{9}.](image)

Boundary scattering naturally also plays a larger role in smaller systems and in systems with rougher surfaces. Reducing the size of the system or roughening its edges are therefore promising routes towards lower thermal conductivity.

### 2.4.2 Temperature dependence

An important value to consider when discussing the temperature dependence of the thermal conductivity and phonon scattering is the Debye temperature, $\theta_D$:

$$\theta_D = \frac{h\nu_D}{k_b},$$

with $\nu_D$ the Debye frequency and $h$ and $k_b$ the Planck and Boltzmann constants respectively.

At low temperatures, $T << \theta_D$, phonon-phonon or impurity scattering rates are low and the mean free path is mainly limited by the boundary of the sample. Under those conditions, $\kappa$ decreases towards zero as the heat capacity does, proportional to $T^3$ according to Debye theory.
At high temperatures, $T > \theta_D$, Umklapp scattering is the dominant process limiting the phonon mean free path $\lambda$. The heat capacity can be regarded as constant at these temperatures, according to the Dulong–Petit law. The thermal conductivity then depends on the temperature in the same way as $\lambda$, namely as $T^{-1}$ [21]. This dependence arises from the linear temperature dependence of the number of excited phonons, as more phonons directly means more scattering. For very high temperatures, above room temperature, it may be that all phonons modes are excited and scattering does not increase further. In that range, $\kappa$ is expected to be constant.

In between the two limiting cases, the thermal conductivity reaches a maximum. An example of the temperature dependence of $\kappa$ is shown in Fig. 5 for bulk indium arsenide with different doping concentrations.

Figure 5: Example of the temperature dependence of the thermal conductivity of bulk InAs. The different numbers refer to different levels of doping. 1: $n=1.6 \times 10^{16}$ cm$^{-3}$, 2: $n=2.0 \times 10^{17}$ cm$^{-3}$, 3: $p=2.0 \times 10^{17}$ cm$^{-3}$. [25]
2.5 Thermal contact resistance

When heat flows through an interface between two different materials, there exists a thermal contact resistance which may affect the measurement of the thermal conductivity of a material. This resistance depends primarily on the contact area between the two materials. However, as no material is perfectly smooth, the contact area is often smaller than it may seem because the two materials only really touch at a finite number of points. This means that rougher materials will give rise to larger thermal contact resistances.

But even at a perfectly smooth surface, there is still some thermal resistance. This is the interfacial thermal resistance that arises from the difference in the electronic and vibrational states in both materials. Because of this difference, a phonon can be scattered at the interface rather than traversing it directly. The probability of that happening depends on the overlap between the phonon states on both sides of the interface, such that a smaller overlap leads to a larger resistance. Consider for example a material that has a very low population of phonons with a certain wavevector. When this material is in contact with another, this means that very few phonons with this wavevector can propagate to the second material. Due to the principle of detailed balance, the reverse is also true and few phonons are transmitted from the second to the first material. This means that the phonons at this wavelength will not contribute much to the conductance.

The interfacial thermal resistance depends on the heat flux, \( Q \), and the temperature difference, \( \Delta T \), as follows:

\[
R_{th} = \frac{\Delta T}{Q}.
\]

(27)

The interfacial contact resistance is typically described by one of two models, the acoustic mismatch model (AMM) or the diffuse mismatch model (DMM). Both of these models ignore electrical contributions to the thermal conductance, so they can only be used when at least one of the materials is an insulator or semiconductor. Both models assume that the materials on either side of the interface behave exactly like bulk material, but they make fundamentally different assumptions about the nature of the interface.

2.5.1 Acoustic mismatch model

In the AMM, the materials in which the phonons propagate are treated as continuous. That is, as having no lattice. The interface is regarded as a perfect plane, at which no scattering takes place. This treatment works best for phonons with wavelengths much larger than the interatomic spacing. Under this assumption, a phonon that is incident on the interface can do two things: reflect or refract. The angles at which this happens obey an acoustic version of Snell’s law for light waves:

\[
v_1 \sin(\theta_{\text{trans}}) = v_2 \sin(\theta_{\text{in}}),
\]

(28)

with phonon velocities \( v_{1,2} \) and angles of incidence or transmission \( \theta_{\text{in,trans}} \). Just as with the optical version of this law, it follows that there is a critical angle of incidence beyond which there can be no transmission as \( \theta_{\text{trans}} \) can not exceed 90°. This critical angle exists only on the side with the smaller phonon velocities. From the other side, all phonons have some probability to be transmitted. If a phonon with incident angle \( \theta_{\text{in}} \) is transmitted with angle \( \theta_{\text{trans}} \) with probability \( \alpha \), then it follows that a phonon incident from the other side with angle \( \theta_{\text{trans}} \) has that same probability to be transmitted under an angle \( \theta_{\text{in}} \). This is a consequence of detailed balance.

It is possible in principle to calculate all the phonon transmission probabilities for each angle, based on an acoustic analog of the Fresnel equations. The gross heat transport can then be found from the sum over all phonon modes. In the simplest picture, the transmission probability can be derived to be:

\[
\alpha_{1\rightarrow2} = \frac{4Z_1Z_2\mu_1\mu_2}{(Z_1\mu_1 + Z_2\mu_2)^2},
\]

(29)

where \( Z_{1,2} \) is the acoustic impedance of the material on either side, equal to the product of phonon velocity and mass density and \( \mu_{1,2} = \cos \theta_{1,2} \). The actual contact resistance can then be approximated
as:

\[ R_{th} = \frac{2}{C_1 v_1 A \int \alpha_{1\to2} (\mu_1) d\mu_1}, \]  

with \( C_1 \) the specific heat of the material from which heat is transmitted \[27\].

### 2.5.2 Diffuse mismatch model

The DMM describes the opposite extreme compared to the AMM. In this model, the assumption of no scattering is replaced with the assumption that all phonons are diffusely scattered at the interface. Every correlation between the incident and transmitted phonons is then destroyed and the transmission probability is set by the phonon density of states and the principle of detailed balance. It does not matter where the incident phonon came from. The DMM typically increases the resistance between solids with similar properties and decreases it between solids with quite different properties, compared to the AMM \[26\].

The phonon transmissivity derived from the DMM is \[27\]:

\[ \alpha_{1\to2} = \frac{C_2 v_2}{C_1 v_1 + C_2 v_2}. \]  

The thermal resistance can then be found as:

\[ R_{th} = \frac{4}{\alpha_{1\to2} C_1 v_1 A}. \]  

### 2.5.3 Previous work on contact resistance

Zhou et al. \[28\] measured the thermal resistance of a nanoscale contact between a SiN\(_x\) membrane and an InAs nanowire. In their work, they compared the thermal resistance of two similar nanowires. One was intact and made good contact with platinum, whereas the other was broken and only made contact at a very small area. The difference in resistance between the two allowed them to extract a contact resistance for the latter of \(6 \cdot 10^8\) K·W\(^{-1}\) at 350 K and estimated contact area between about 70 and 350 nm\(^2\).

Calculations with the DMM yielded values 2 or 3 orders of magnitude smaller than the measured resistance however. This was attributed to an overestimation of the transmissivity due to the presence of a native oxide or a weak interface bonding. Their findings suggest that thermal contacts can be a large source of error in thermal measurements of individual nanowires, and they need to be examined carefully.

Theoretical calculations by Prasher \[29\] show the effect of a weak interface bonding. The traditional AMM assumes a perfectly welded contact between the two materials, leading to continuity of stress and displacement at the interface. A nanowire lying on a substrate is typically only bound by weak van der Waals forces however and this assumption is not valid. The difference can be accounted for by including an additional term in the calculation of \(\alpha_{1\to2}\). For very weak bonding, the transmissivity can then become orders of magnitude smaller.
2.6 Electrical conductivity

The electrical conductivity $\sigma$ measures how well a material can conduct a current. The inverse of the conductivity is the resistivity. In a semiconductor, electrons in the conduction band and holes in the valence band are responsible for carrying an electrical current. As the temperature increases, additional electrons are thermally excited from the valence band into the conduction band and thereby the conductivity increases and the resistivity decreases. For an undoped, crystalline semiconductor, the temperature dependence of the resistivity $\rho$ then becomes:

$$\rho = \frac{1}{\sigma} = \rho_0 e^{\frac{E_g}{k_b T}}, \quad (33)$$

with $E_g$ the bandgap of the semiconductor.

Doped semiconductors typically have increased conductivity compared to intrinsic semiconductors as more charge carriers are available. Very highly doped semiconductors can even behave like a metal. For a metal, many electrons are available to carry a current, giving it a high conductivity. When the temperature is increased, the conductivity of a metal decreases as more scattering takes place.

The resistivity can also be related to the mobilities, $\mu$ and densities of charge carriers.

$$\rho = \frac{1}{q(n\mu_n + p\mu_p)}, \quad (34)$$

with electron density $n$, hole density $p$ and charge $q$. 
3 Nanowires

This chapter contains a mix of theory and experiment. The advantages of nanowires for thermoelectrics are first explained in Sec. 3.1. The reasons why InAs nanowires are chosen are mentioned in Sec. 3.2 and the process of growing nanowires is described in Sec. 3.3. In Sec. 3.4 an overview of the results of other work on InAs nanowires is given. The process used to etch the wires is described in Sec. 3.5, and finally Sec. 3.6 concerns the surface roughness of the nanowires.

3.1 Introduction to nanowires

There are two main advantages of nanowires as thermoelectric material. The first is an increased boundary scattering compared to bulk. This effect becomes increasingly prominent as the wire gets thinner, simply because the surface of the wire then becomes a larger part of the system.

The second advantage appears only for very thin wires. Once the system behaves as a onedimensional conductor, there can be an increase in the power factor, $S^2 \sigma$. This increase has long been predicted to arise as a result of the discontinuous electronic density of states (DOS) associated with onedimensional quantum confinement.

This can also be seen from Mott's formula (Eq. 2). As the DOS is discontinuous, the derivative becomes very large and the Seebeck coefficient is enhanced. The effect of reduced dimensionality on the DOS is illustrated in Fig. 6.

In order to benefit from the increased DOS, the nanowire needs to be gated to place the Fermi level at the position of singular DOS. It has proven experimentally very difficult to demonstrate the predicted increase of power factor however. This has to do with the fact that nanowires are typically too large, so that low temperatures and carrier concentrations are required in order to reach the regime of 1D electron transport. Additionally, even if this regime is reached there may still be defects that dominate electrical transport. Despite this, Tian et al. [31] found the first evidence of this effect in gated InAs wires in 2012.

To profit from the effect of boundary scattering, it is also beneficial to access the regime of 1D electron transport. With the electrons moving only parallel to the wire axis, they can not scatter off the surface and electron mobility remains unchanged [2]. Phonons still move in three dimensions at this point however, so they can scatter off the surface. In this way, the lattice thermal conductivity is reduced, while the electronic conductivity is not.

The reduction of the thermal conductivity is then especially great if the wire diameter is smaller than the phonon mean free path. There will still be a reduction in thermal conductivity even at larger diameters, but if the condition of 1D electrical transport is not satisfied the electrical conductivity may also be reduced.
3.2 Indium arsenide nanowires

The nanowires used in this project are made of indium arsenide (InAs). One advantage of InAs is that it should in principle be easy to contact electrically due to the presence of a conductive surface layer. This layer arises from pinning of the Fermi level inside the conduction band \[32\] and causes metallic contacts to InAs to be typically ohmic without Schottky barriers.

There have been theoretical studies of different materials that could work for thermoelectrics. Mingo \[33\] calculated the expected maximum $ZT$ and power factor of four types of III-V semiconductor nanowires. Based on his calculations, only indium antimonide (InSb) is potentially attractive for a practical application, while GaAs or InP are of no use. InAs is in between. Neither the bulk properties nor the potential enhancement for nanowires are quite as good as for InSb, but they are much better than for GaAs or InP. The main results of Mingo are shown in Fig. 7.

![Figure 7: Results from the paper of Mingo \[34\]. a) Calculated lattice thermal conductivity versus wire diameter $L$ for four types of III-V semiconductor nanowires, with diffusive (thick lines) or partially specular (thin lines) phonon boundary scattering. Inset: crossover between electronic (thin lines) and lattice (thick lines) thermal conductivity. Circles mark the crossing points. b) Calculated $ZT$ vs wire diameter. Inset: $ZT$ with diffusive boundary scattering, in logarithmic scale.](image)

The bulk values of the thermoelectric properties of InSb and InAs have already been investigated for potential applications decades ago \[35\] and they are better than those of other III-V materials.

An additional advantage in the case of nanowires arises from the small effective electron mass, $m^*$, in both these materials. Mingo observed a sharp increase in the power factor in nanowires with diameters below a certain value. This onset diameter was found to be approximately proportional to $1/\sqrt{m^*}$. Considering that the electron wavelength is also proportional to $1/\sqrt{m^*}$, this is not surprising. The onset diameter describes the point where the system size is of the same order as the electron wavelength, and the system begins to act as a onedimensional conductor. This means that the benefit of reducing diameter occurs sooner in materials with small $m^*$, such as InSb and InAs. The small $m^*$ also leads to
larger 1D sub-band splitting, meaning that 1D confinement effects can potentially be studied at relatively high temperatures [31].

One might wonder why InAs is studied in this work, and not InSb while it is predicted to be much better. This has to do with the easier contacting mentioned earlier, but also with the growth of the nanowires. The growth of InSb wires that are long enough for thermoelectric measurements is more difficult than that of InAs wires. Additionally, it is easier to grow InAs wires with small diameters. This motivates the choice to work on InAs wires first. The aim is then to demonstrate a diameter dependence of the properties of these wires, which can serve as a model system for other wires. It is not expected that InAs nanowires will directly find an application in thermoelectrics.
3.3 Growth of InAs nanowires

The nanowires are grown by metal organic vapor phase epitaxy (MOVPE) using the vapor–liquid–solid (VLS) mechanism. The VLS mechanism uses a catalytic droplet to mediate growth and takes place under a flow of precursor materials in vapor phase. The precursor materials are cracked at the surface of the droplet and the droplet then absorbs specimen atoms until it is supersaturated, at which point crystal growth will start at the liquid–solid interface.

In this case, the growth starts on an InP 111B substrate on which gold colloids are deposited. The substrate is heated so that the solid gold particles become liquid droplets. At first a short InP stem is grown to improve nucleation, and then the growth conditions are changed to start InAs growth. This is done under a flow of precursors trimethylindium (TMIn) and arsine (AsH$_3$).

In addition to the vertical VLS growth, there is often also another kind of growth happening on the sidewalls of the nanowire. This is due to vapor–solid (VS) growth. VS growth often causes the nanowire to be tapered and is thus undesirable. The VS grown part of the wire also tends to have increased incorporation of carbon atoms. The whole growth process is illustrated in Fig. 8.

![Figure 8: Illustration of the VLS growth mechanism used for InAs nanowires.](image_url)

Nanowires from five different growth series were used in this work. An SEM image showing a section of a sample from one of these series is shown in Fig. 9. InAs is quite sensitive to growth conditions such as temperature and precursor flow, so the properties of the wires may vary between growth series. The conditions for each series can be found in appendix A.
InAs nanowires can be grown with two different crystal structures, wurtzite (WZ) and zinc blende (ZB). An image of the unit cells of both these structures is shown in Fig. 10. The WZ structure is hexagonal and consists of two stacked crystal planes A and B. ZB on the other hand is a cubic crystal structure with three different planes in ABC stacking. The differences between the WZ and ZB structures may also induce differences in their thermoelectric properties, especially if a nanowire has stacking faults so that it includes both WZ and ZB. This makes it necessary to be aware of the structure of any measured wire. In this project, the wires are all wurtzite with few stacking faults.

Figure 10: Illustration of the unit cell of the A) wurtzite and B) zinc blende crystal lattices.
3.4 Previous experiments on InAs nanowires

There have been several other studies on the thermoelectric properties of InAs nanowires. Most of these focus either on measuring the thermal conductivity or the electrical properties and Seebeck coefficient. A study by Mavrokefalos et al. [5] stands out as they are able to measure $\kappa$, $\sigma$ and $S$ on the same wire, and additionally characterize the structure and composition of that wire with transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX). The device used in their experiments is similar to the one used in this work, but also has a hole in the substrate below the device that allows for TEM measurement.

For an InAs nanowire with rectangular 150x40 nm cross section, they report $\kappa=4.11 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$, $S=-57.2 \mu\text{V} \cdot \text{K}^{-1}$, $\sigma=1350 \text{ S} \cdot \text{m}^{-1}$ and $ZT=0.00032$ at a temperature of 300 K. Since these wires are prepared in a different way as the ones measured in this work, they are not necessarily similar.

Very recently, another report has been published of a study that included measurements of all three thermoelectric properties [7]. Averaged over about 10 different wires, they found $\kappa=2.5 \pm 1 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$. As evidenced by TEM, the wires in their study have a large number of stacking faults, which are likely to lower the thermal conductivity compared to a pure material. They additionally reported a power factor $\sigma S^2=4.6 \mu\text{W} \cdot \text{K}^{-2} \text{m}^{-1}$ and $ZT=5.4 \cdot 10^{-4}$ at 300 K.

In most other work with the same type of device, only the thermal conductivity was measured. This was also done with InAs nanowires by Zhou et al., who compared wires with zinc blende (ZB) and wurtzite (WZ) structures. Their results for WZ wires are comparable to those of Mavrokefalos, whereas those for ZB wires were somewhat higher. The data from both Zhou and Mavrokefalos are shown in Fig. 11.

![Figure 11: A) Results from the work of Mavrokefalos et al. [5]. B) Results from the work of Zhou et al. [3].](image-url)
The thermal conductivity of InAs nanowires has also been measured with other methods. Persson et al. [4] used time-domain thermoreflectance (TDTR) on nanowire composites consisting of arrays of InAs nanowires embedded in PMMA. In TDTR measurements, short laser pulses are split into a pump beam and a probe beam. The pump beam is used to heat the sample, creating an abrupt temperature rise at the surface for each pulse. The probe beam then measures the thermoreflectance, that is the change of the reflectivity with temperature, of an aluminum film deposited on top of nanowire composite. From this the thermal conductivity can be extracted. With this method, they found $\kappa = 5.3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for 52 nm diameter wires, in reasonable agreement with the other results.

Karg et al. [6] used yet another method to determine thermal conductivity. They measured the electrical resistance of an InAs NW as a function of applied current for different substrate temperatures. They fabricated four contacts on a nanowire lying on a substrate as well as a heater at one end. They then etched away the substrate right below the wire. From the temperature dependence of the nanowire resistance, they then extract the thermal conductivity. They find a value of only $2.1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for $\kappa$ for diameter of 100 nm, which is significantly lower than most other measurements. This deviating value indicates that the thermal conductivity can vary significantly between different wires, particularly if they have many stacking faults.

What all these experiments have in common is that only a single one or a small number of wires with different diameters is measured. There is no comprehensive experimental study of the thermal conductivity for different diameters. As significant changes have been predicted for decreasing diameters, it is interesting to perform precisely such a study.

Unlike on the thermal conductivity, there has been work on the diameter dependence of the electrical conductivity. Scheffler et al. [37] studied this by contacting multiple sections of tapered wires and measuring the properties of each section. At room temperature, they found a diameter-independent conductivity of approximately 5000 $\text{S} \cdot \text{m}^{-1}$ for diameters larger than 40 nm. For diameters below 40 nm, the conductivity did decrease considerably. This is not a good thing for thermoelectrics, but it may be compensated for by an increased Seebeck coefficient or decreased thermal conductivity. The mobility that they found was $4000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.

There have also been several studies measuring the Seebeck coefficient or the thermopower of InAs nanowires [38–40]. It is difficult to compare their results, as they are all measured with different levels of doping, gate voltages and temperatures. One study demonstrates the effect of a peaked 1D density of states [31] in nanowires of approximately 20 nm in diameter, which is of particular interest for thermoelectrics.
3.5 Citric acid: $\text{H}_2\text{O}_2$ etching

Getting access to a wide range of diameters through growth is difficult and time consuming. Therefore, the wires are etched to reduce their diameter. The etching process is based on the work of Dier et al. [41], who found that InAs can be etched by a solution of citric acid and hydrogen peroxide. They measured an etching rate of about $93 \text{ nm} \cdot \text{min}^{-1}$ on bulk InAs. Since the bulk material is zinc blende and the nanowires are wurtzite, the etching process can be different.

To adapt this procedure for the WZ InAs nanowires, a number of tests was done. In order to have reasonable statistics, the diameters of 50 wires on an as-grown sample were measured with SEM. Then, a citric acid solution of $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O} = 1 \text{ g} : 1 \text{ ml}$ was mixed with hydrogen peroxide ($\text{H}_2\text{O}_2$) in a 50:1 ratio and stirred for two minutes. The as-grown sample was submerged in the solution for some time, rinsed with water, dried and then measured again with SEM. It was found that the same wires that had been previously measured with SEM were not etched, while others were. From this, it appears that the SEM deposits a layer of probably carbon on the surface of the wire, preventing etching. After measuring the diameters of 50 other wires on the same sample, an average etching rate could be determined, but not with good accuracy. The measured rate was: $1.8 \pm 1.1 \text{ nm} \cdot \text{s}^{-1}$. Note that this is the rate at which the wire diameter decreases, not the rate at which InAs is etched from a surface.

For very long etching times of minutes, only possible on thick microwires, the etching appeared to have no more effect after about five minutes. The reason for this is unknown, but may be related to a layer that forms on the wire. It can be clearly seen on SEM images that there are drops of material sticking to the surface of these long-etched wires, see Fig. 12.

![Figure 12: Example of a microwire that has been etched for several minutes.](image)

It was also observed that wires will be drawn together when dried in air, as shown in Fig. 13. This is due to capillary forces and it can be prevented by using a critical point dryer (CPD) to dry the sample after rinsing it. The effect is particularly bad for high density nanowire samples.
Figure 13: Example of the effect of capillary forces on an as-grown sample of nanowires after drying to air.

For the critical point drying process, the sample needs to be placed in acetone in the CPD chamber. The acetone is being used because it has a low surface tension and is miscible with liquid CO$_2$. Inside the CPD chamber, the acetone is replaced with liquid CO$_2$ in several flushing steps. After that, the pressure and temperature are changed past the critical point of the CO$_2$. When there is no more liquid left, the CO$_2$ can be brought to its gas state and the pressure is reduced to atmospheric levels so that the chamber can be opened and the sample removed. During this process, the sample does not experience any rapid transition from wet to dry and does not suffer from capillary forces.
3.6 Surface roughness

The surface roughness of the nanowires may have a large effect on its thermoelectric properties. A rougher surface will cause more scattering and can therefore reduce thermal conductivity. This makes it important to determine what is the roughness of all the measured nanowires. This can be done with atomic force microscopy (AFM), but only on wires that have been transferred to a flat surface.

It is not possible to measure the roughness and the thermal conductivity on the same wire. This is because AFM measurements of a wire on a suspended device cause the device to vibrate and only a heavily distorted image can be made. It is also not possible to pick up a wire that has been measured with AFM and place it on a device for thermal measurement, as it is usually stuck to the substrate and may also be damaged by the AFM. Wires that are already placed on a device stick to it as well, and thus the reverse process of taking a measured wire from a device to a substrate for AFM is not feasible either.

The AFM images are taken in tapping mode, meaning that the cantilever oscillates up and down near resonance. The image is produced by imaging the force when the tip touches the surface. In principle this method should be non-destructive, yet it is sometimes observed that wires move or break while imaging. On rare occasions they will even stick to the AFM cantilever. Because of these issues, it is difficult to acquire a large number of images of different wires. Most measurements of the roughness are therefore averaged over only two or three nanowires. A typical AFM image is shown in Fig. 14.

![Figure 14: Typical AFM image of an InAs nanowire.](image)

The root-mean-square roughness along a line over the nanowire surface can be extracted from the image with the Gwyddion SPM data analysis software. This roughness is found to be between 0.29 and 0.67 nm for all wires, which is less than or comparable to the lattice constant of InAs. Whether the wires are from different growth series or have been etched makes no apparent difference. Because of this, the roughness can be eliminated as a factor when comparing the thermal conductivities of different nanowires.
4 Experimental methods

This section serves to describe the setup of the experiments and how they are done. First, the device and its fabrication are discussed in Sec. 4.1 and then the setup used to measure with it in Sec. 4.2. A thorough derivation and description of the measurements are given in Sec. 4.3 while the sensitivity and possible errors are discussed in the following two sections, 4.4 and 4.5.

4.1 Devices

The devices that are used in this project are based on those used by Shi et al. They consist of two suspended 20x20 µm SiN$_x$ membranes, each supported by six 3 µm wide SiN$_x$ beams. On each membrane there is a platinum coil that acts as a platinum resistance thermometer (PRT). Four platinum lines are connected to each coil and allow for a four-point measurement of the resistance. Each membrane additionally has two platinum electrodes meant for four-point electrical measurements of a nanowire.

Different versions of this device exist and are used by other groups. Some of these have a smaller number of contacts, and therefore less legs, others even use just two legs per membrane and have multiple electrical lines on one beam. The most advanced versions even include a hole that goes through the entire chip. The hole is located below the membranes and thereby allows for TEM measurements of wires while on a device. There are no such holes in the devices used for this work.

The platinum lines follow the SiN$_x$ beams up to the point where they are connected to the substrate. There, the lines branch out and are connected to large platinum pads which can be contacted. Often there is some misalignment between the platinum and SiN$_x$, causing the coils to not be centered on the membrane. An SEM image of the device is shown in Fig. 15.
Figure 15: Tilted SEM image of a typical device with a single nanowire. A small pyramid can be seen under each membrane. These are simply leftovers from the fabrication process.

The SiN\textsubscript{x} is approximately 450 nm thick and the beams are 3 \( \mu \text{m} \) wide and 449.5 \( \mu \text{m} \) long by design. The thickness of the Pt is 30 nm, and the Pt lines are 1 \( \mu \text{m} \) wide. The cross-sectional area of a beam is then 1.35 \( \mu \text{m}^2 \) of SiN\textsubscript{x} and 0.03 \( \mu \text{m}^2 \) of Pt. Bulk thermal conductivities for these materials are 5.5 and 71.6 W\( \cdot \text{m}^{-1}\text{K}^{-1} \), respectively, so the total conductance of one beam should be about 21 nW\( \cdot \text{K}^{-1} \). Combining all the beams on one membrane, that makes 127 nW\( \cdot \text{K}^{-1} \). Since the shape of the beam is not exactly rectangular, the thickness of the SiN\textsubscript{x} is not exactly known and the conductivity can be different from the value in literature, this value for the conductance should be taken as a rough estimation rather than an accurate calculation.

4.1.1 Device fabrication

Fabrication of the device starts from a Si[100] substrate. A 607 nm layer of SiN\textsubscript{x} is grown on top of it using plasma enhanced chemical vapour deposition (PECVD) in a parallel plate reactor. In this process, a plasma is created between two parallel plates that breaks the bonds in precursor materials. The plasma is created by applying an AC voltage between the two plates, causing the surface of the sample to be bombarded with ions that will form the SiN\textsubscript{x} layer.

The composition and characteristics of the SiN\textsubscript{x} can be controlled by a combination of two different frequencies for the AC voltage. A higher frequency will give more energy to the electrons, while the ions will follow a lower frequency. This lower frequency causes the ions to be implanted further into the film, causing a higher packing density and thus more compressive strain. The ions then also introduce energy to the surface, reducing the tensile strain. The high frequency PECVD on the other hand generally
causes tensile strain. A stress free material can be created by choosing the right combination of high/low frequency pulses.

The next step is the creation of the Pt pads and lines. The big pads and lines are defined first with optical lithography in an MA6 contact aligner. Before the optical resist is spun, several steps are taken to clean the sample and a layer of HDMS is deposited to ensure good adhesion of the resist to the substrate. Optical resist MaN-415 is spun at 3000 RPM for 30 seconds and then baked at 95 °C for 6 minutes to remove all solvents from the resist layer and prevent moving of the resist. MaN-415 is a negative photoresist, which is beneficial as it causes a natural slope in the resist profile after illumination and development, helping the lift-off process.

After the exposure, Ma-D 332s is used to develop the resist. Then, the sample is placed in an e-beam evaporator for the Pt deposition. This machine will create a flux of atoms towards the sample by evaporating them using heating from accelerated electrons. For lift-off, the sample is first kept in acetone vapor for about one hour. When cracks start appearing, it is placed in the acetone for one minute and then sonicated for approximately 30 seconds. IPA is used afterwards to clean off any remaining acetone.

The coils are too small to be defined with optical lithography, so electron beam lithography (EBL) is used instead. EBL makes it possible to define much smaller features, and also allows for some flexibility as the design can be quickly changed. The sample is first cleaned and then PMMA-A4 resist is spun at 9000 RPM for 60 seconds. It is then baked for half an hour at 200 °C. For the exposure, a 20 kV acceleration voltage was used with a 10 µm aperture. Due to a small overdose, the width of coils turns out larger than designed, i.e. 125 nm.

The developer for PMMA-A4 is MIBK:IPA 1:3, which is used for 70 seconds. The sample is then rinsed with IPA and placed in a 100W O2 plasma for 10 seconds to remove any residues on the surface. After that, the Pt is deposited in the same way as before. The lift-off needs to be done more carefully now as the coils are sensitive to be washed away. To that end, the sample is not sonicated and the resist is instead blown away with a pipette. At this point, the device will look as in Fig. 16A.

Next, another 300 nm layer of SiNx is deposited with PECVD. This is done to protect the Pt during the coming fabrication steps. The SiNx beams are then defined with optical lithography in a similar process as the pads and lines. A different resist is used this time however, namely the positive resist HPR504. After spinning under the same conditions as the MaN-415, the resist is baked for 2.5 minutes at 100 °C. After the exposure, the resist is baked again for 2.5 minutes, but this time at 115 °C. This serves to further strengthen the resist layer before development, which is done for 75 seconds.

The sample is then etched with reactive ion etching (RIE). This process etches both the SiNx and the resist, but does the former at a much higher rate (110 mm/min compared to 65 mm/min). When the SiNx is etched all the way through, the Si substrate is also etched a little. The RIE process leaves a thin layer of reaction products, which have to be cleaned off with O2 plasma cleaning and HF(1%) before wet etching can take place.

The wet etching to create the undercut of the device is done with 2.38 % tetramethylammonium hydroxide (TMAH) at 80 °C. The etchant includes surfactants as well, since an AZ 826 MIF developer solution is used. The alkaline character of the substances causes the OH− group to bind to the silicon. The resulting silicic acid is dissolved in the etching solution. This etching is isotropic and takes six hours to create the undercut of approximately 10 µm.

The device then looks like Fig. 16A, with a Si mountain under each of the SiNx membranes. These need to be removed to be sure the device is really suspended. To do that, the sample is anisotropically etched in a 33% KOH solution for five minutes. The sample is then again rinsed with water. To dry the sample, it is first placed in IPA at 80 °C and then held above it in IPA vapor to dry. The IPA has a lower surface tension than water, which reduces the capillary forces on the device so that the bridges are not pulled to the side. The device then looks as in Fig. 16B.
Finally, there may still be some SiN\(_x\) remaining on the surface, making it impossible to contact the Pt pads. If that is the case, the sample has to be etched again with RIE until all SiN\(_x\) on the Pt is removed. It is immediately clear whether this has been done successfully when an attempt is made to contact the pads. When it has, the device is ready for wire placement and measurements.

### 4.1.2 Wire placement

Nanowires need to be placed on the membranes such that they bridge the gap between them, but ideally not such that they also touch the coils. If they do touch the coils, there is a possibility that they will make electrical contact there, which would interfere with the measurements. Fortunately, this is not probable.

In order to place a wire, a Kleindieck micromanipulator with a tungsten tip is used to pick up a single wire from an as-grown sample. These manipulators contain three piezoelectric stick-slip motors that allow the tip to move in every direction as well as rotate around its own axis. The InP stems on which the InAs wires are grown provide a natural point where the wire will break off of the substrate. Once a wire is stuck to the tip, it can be transferred to the device and placed in any desired position. This whole process is done under an optical microscope, mostly using a 10 times magnification, but some times also 100 times.

The device and nanowire transfer method place some constraints on the growth and processing of the nanowires. First of all the distance between the membranes requires that the wires are longer than 10 \(\mu m\), but preferably not longer than 20 \(\mu m\), lest they touch the coils. The distance between the wires on the as-grown surface also can not be too small, or it becomes very difficult to pick up just one wire. Furthermore, if the wires are etched, they can not be dried in air or capillary forces will draw them together. If that happens it also becomes very difficult to pick up a single wire. Often a whole bundle of wires will be picked up instead, while the difference is not always possible to see with optical microscopy.

### 4.1.3 Electron beam induced deposition of platinum

For some measurements, platinum is deposited on the membranes so that it covers a section of the wire on either side. This is done in order to improve the thermal contact between the wire and the membrane and to create an electrical contact if possible. The platinum is deposited with electron beam-induced deposition (EBID) at a voltage of 30 kV and a current of 0.16 nA.

A FEI dualbeam system is used for the EBID process. The sample is placed inside a high vacuum chamber with a scanning electron microscope (SEM). Precursor material is sublimated and introduced into the chamber while the SEM is used to scan over the desired area for the deposit. Secondary electrons that are emitted after absorption of the primary electrons then break the molecular bonds of the precursor molecules and cause deposition of the material. The primary electrons from the SEM have an energy that is too high to break the bonds.
This process is far from clean. In fact, only about 16% of the deposited material will actually be platinum. The rest will be composed of carbon and oxygen. This does not help the electrical properties, but it is not a problem for the thermal contacts. Even if the deposited material is of very low quality, it will still improve thermal contact.

In principle the accuracy of EBID is very good and deposition can occur with nanometer resolution. However, if the SEM is used to view the device after the deposition, there may still be leftover precursor material that can decompose and be deposited on the wire. This is undesirable, as a layer of material deposited on the section of wire between the two contacts can affect the measured properties. Therefore, observation of the wire needs to be avoided after the deposition process.

The EBID method is often used to improve thermal contacts to single nanowires. Mavrokefalos et al. \cite{5} used it as well and afterwards observed their wires with EDX. In this way, they were able to check the composition of their wires after the deposition. They found no sign of platinum on their wires, showing that EBID does not significantly contaminate the nanowire.
4.2 Measurement setup

The device is placed in a probestation that is equipped with two opposing probe arms with six tips each, that can be used to make electrical contact to the device. The tips on each arm can not be moved independently, but are aligned so that they will contact six adjacent pads when placed correctly, even when not all six are being used in the measurement.

A Keithley 4200 Semiconductor Characterization System (SCS) is used to apply and measure voltages and currents as necessary. The SCS has four pairs of connections available, with each pair consisting of a force and a sense connection. Both of these can serve in the same way, but the sense connections have a much higher input impedance. In effect, this means that when both are connected, current will only flow through the force connection while the sense measures the voltage. An illustration of the use of force and sense connections to measure the voltage across a coil is shown in Fig. 17.

![Figure 17: Schematic of the measurement of a voltage across a coil, using force and sense connections.](image)

Connection 1 is programmed to supply a current and measure it while also measuring a voltage. With both the force and sense connected, this current will be supplied through the force connection. Connection 2 is programmed to measure a current and maintain the voltage at 0 V. As the sense connections have a high input impedance, the current supplied by force 1 can only flow towards force 2. The current is then measured at both force 1 and force 2 and is the same at both locations except for a minus sign. In this scheme, no current enters the sense connections. The voltage at sense 2 is equal to zero, so the voltage measured by sense 1 is the voltage across the coil. In any case, the voltage is measured relative to the internal reference voltage of the Keithley SCS.

A LakeShore 336 temperature controller can heat the system and liquid nitrogen or helium can be used to cool it. At 320 K or higher, the controller can keep the system temperature stable to within a few mK. Closer to room temperature however, the stability is much worse and the system temperature can have fluctuations larger than 100 mK. When the setpoint is 300 K for example, the actual system temperature can deviate by as much as 300 mK. During measurements at room temperature, the controller is not used and system temperature remains stable within a few mK.

Before any thermal measurement, the probestation is pumped down to a pressure below $10^{-5}$ mbar. It is important that the pressure is low enough before any measurement of the thermal conductivity, as a significant conduction by air would interfere with the measurement.
4.3 Description of the experiments

In order to measure the thermal conductivity, a heating current $I_h$ is sourced through the coil on one side of the device. This current causes a joule heating of:

$$Q_h = I_h^2 R_h,$$  \hspace{1cm} (35)

with $R_h$ the electrical resistance of the coil.

On the other membrane, a smaller sensing current $I_s$ is applied to the coil in order to be able to measure the resistance $R_s$. Joule heating due to this current is very small and can be safely neglected.

The voltage across the coils on both sides is also measured and their resistances can be calculated using Ohm’s law. A schematic of this experiment is shown in Fig. 18.

![Diagram of the measurement of the thermal conductivity](image)

Figure 18: Schematic of the measurement of the thermal conductivity. Various quantities are indicated that are explained in the text. The red arrows represent heat flows.

In order to determine the thermal conductivity of the nanowire, all the heat that is generated and flows through the device and the wire needs to be considered.

The total heat that is produced in the heating membrane is equal to $Q_h$ plus the joule heating, $Q_L$, in the two platinum lines that supply the current to the heating coil.

$$2Q_L = 2I_h^2 R_L,$$  \hspace{1cm} (36)
with $R_L$ the resistance of a platinum line.

Assuming that the conduction of heat through air and radiation is negligible, the heat can only leave the system through the beams that support the membranes. As long as the vacuum level is good and the temperature change is not too large, this assumption is justified.

Now, the heat conduction to the environment through the two beams that provide the current to the heating coil can be derived from the heat-diffusion equation in steady state:

$$
\frac{Q_L}{L_b} = -\kappa_b A_b \frac{d^2 \Delta T}{dx^2},
$$

with $L_b$, $A_b$ and $\kappa_b$, the length, area and thermal conductivity of a beam and $\Delta T_h = T_h - T_0$ the difference in temperature between the heating membrane and the bath. The position along the beam is called $x$. With the boundary conditions $\Delta T(x = 0) = 0$ and $\Delta T(x = L_b) = \Delta T_h$, the solution becomes:

$$
\Delta T(x) = -\frac{Q_L x^2}{2 L_b \kappa_b A_b} + \left( \frac{\Delta T_h}{L_b} + \frac{Q_L}{2 \kappa_b A_b} \right) x.
$$

This is the temperature profile along one of the heating beams. From this, the heat flow to the environment can be determined:

$$
Q_{h,2} = 2 \kappa A_b \left( \frac{\partial \Delta T}{\partial x} \right)_{x=0} = 2 \left( \frac{G_{b1} \Delta T_h}{6} + \frac{Q_L}{2} \right),
$$

with the factor of 2 coming from the fact that there are two beams that carry a heating current. $G_{b1}$ is the thermal conductance of all six beams beams on this side, so for a single beam it is $G_{b1}/6$.

The other four beams on this side simply give:

$$
Q_{h,4} = \frac{4 G_{b1} \Delta T_h}{6}.
$$

Neglecting the heating due to $I_s$, the heat leaving through the six beams on the sensing side is:

$$
Q_{s,6} = G_{b2} \Delta T_s,
$$

with $\Delta T_s = T_s - T_0$ the temperature difference between sensing membrane and environment, and $G_{b2}$ the beam conductance.

Equating the amount of energy that enters and leaves the system then gives:

$$
Q_{h,2} + Q_{h,4} + Q_{s,6} = G_{b1} \Delta T_h + Q_L + G_{b2} \Delta T_s = Q_h + 2Q_L,
$$

or

$$
G_{b1} \Delta T_h + G_{b2} \Delta T_s = Q_h + Q_L.
$$

In other work with similar devices, it was tacitly assumed that $G_{b1} = G_{b2} = G_b$ as the beams that support both membranes are designed to be identical. Under this assumption, the beam conductance becomes:

$$
G_b = \frac{Q_h + Q_L}{\Delta T_h + \Delta T_s}.
$$

The conductance of the nanowire can then be readily determined by considering the heat that is conducted through the wire towards the sensing membrane and the heat that is conducted from there to the environment, such that:

$$
G_b \Delta T_s = G_s (\Delta T_h - \Delta T_s),
$$

with $G_s$ the conductance of the nanowire sample.

If the beam conductances are not assumed to be equal, the analysis becomes more complicated and another assumption is required to be able to determine the wire conductance. Eq. 43 can be rewritten as:

$$
G_{b2} = \frac{Q_h + Q_L}{G_{b1} \Delta T_h + \Delta T_s}.
$$
The wire conductance then becomes:

$$G_s = \frac{(Q_h + Q_L)\Delta T_s}{\left(\frac{G_{b1}}{G_{b2}}\Delta T_h + \Delta T_s\right)\left(\Delta T_h - \Delta T_s\right)}. \quad (47)$$

Now consider the situation where the other membrane is heated. Eq. (43) becomes:

$$Q_h' + Q_L' = G_{b2}\Delta T_h' + G_{b1}\Delta T_s' = G_{b1}\left(\frac{G_{b2}}{G_{b1}}\Delta T_h' + \Delta T_s'\right), \quad (48)$$

such that:

$$G_s' = \frac{(Q_h' + Q_L')\Delta T_s'}{\left(\frac{G_{b1}}{G_{b2}}\Delta T_h' + \Delta T_s'\right)\left(\Delta T_h' - \Delta T_s'\right)}. \quad (49)$$

To find the conductance of the nanowire, it must now be assumed that $G_s = G_s'$. This must be true as long as there are no nonlinearities in the system, such as for example a temperature dependence of the conductivity. Eqs. (47) and (49) can then be used to find the ratio $G_{b1}/G_{b2}$ as well as the wire conductance. The solution of this equation is a formidable expression and can be found in appendix C.1.

### 4.3.1 Temperature coefficient of resistance

$\Delta T_h$ and $\Delta T_s$ can be determined by using the coils as resistance thermometers. This requires an accurate knowledge of the temperature coefficient of resistance, $\alpha$:

$$\alpha = \frac{1}{R} \frac{dR}{dT}. \quad (50)$$

As the coefficients of both coils vary slightly from one device to another, a new calibration has to be made for each experiment. This is done by measuring the resistances right before each experiment to measure the thermal conductance. The resistance of both coils is then measured at the system temperature, before one of the coils is heated. For a whole series of measurements, this system temperature is usually varied between room temperature and 360 K.

Since the relation between resistance and temperature is linear, $dR/dT$ can be found as the slope of a linear fit. The $R$ in Eq. (50) is the one that was measured at each temperature, so that $\alpha$ itself is temperature dependent. However, $\alpha$ will not only vary as the system temperature changes, but also as the coils are heated. For larger $\Delta T_h/\Delta T_s$, the value of $\alpha$ therefore becomes less reliable.

A typical example of the measurement of $\alpha$ is shown in Fig. 19A. In this case, the slopes are about 25 $\Omega\cdot K^{-1}$. The resulting values of $\alpha$ then vary between 1.47 and 1.65$\cdot 10^{-3}$ K$^{-1}$ as seen in Fig. 19B. These values are less than half the bulk value and in reasonable agreement with reported values for thin films [45].
Figure 19: A) A typical result of the measurement of the temperature coefficient of resistance. The black and blue points are measured for the two membranes of one device. The lines are the result of a linear fit through this data. B) The resulting $\alpha$ as a function of temperature.

The actual temperature changes can be calculated as follows:

$$\Delta T_{h,s} = \frac{1}{\alpha} \frac{\Delta R_{h,s}}{R_{h,s}},$$

where $R_{h,s}$ is the resistance measured at the start of the measurement on either membrane and $\Delta R_{h,s}$ is the change of the resistance relative to $R_{h,s}$.

### 4.3.2 Determination of the applied power

Experimentally, the heat that is generated in the coil and the lines can be determined from the applied current and the resistances of coil and lines. The former can be determined with a four-point measurement as shown in Fig. 18. The latter requires both the four-point measurement and also a two-point measurement where the voltage is measured at the same leads through which the current flows. The resistance of these two lines can then be found by subtracting the four-point from the two-point resistance. The total power applied to the system is then found as:

$$P = Q_h + Q_L = I_h V_h \left( 1 + \frac{R_L}{2R_h} \right),$$

for every measured voltage, $V_h$, across the heating coil with resistance $R_h$. $R_L$ is the resistance of the two lines that generate a total heat of $2Q_L$. The factor of 2 in Eq. 52 then arises from the fact that only half of the heat from the lines contributes towards heating the system, and the other half is just conducted to the environment, as shown in Eqs. 38 and 39.

The resistances of the lines and coils, necessary to determine $\alpha$ and the applied power, are all measured at the start of each experiment. This is done by ramping both $I_h$ and $I_s$ from -20 to 20 nA and measuring the voltage. The slope of a linear fit through this data then gives the resistance while the intercept gives an offset voltage that needs to be corrected for in the thermal conductance measurement. Doing this in a four-point configuration gives the coil resistance, and two-point gives the coil plus line resistance. From these measurements, the resistances of both coils and of the lines going to both coils are obtained.

The offset voltage is usually less than 0.1 mV, which is small compared to the measured voltages, but large enough that a correction is in order. The reason for this offset voltage is also a thermoelectric effect. It arises when different parts of the system are at different temperatures and made of different materials.
4.3.3 Execution of the experiment

In the main experiment, \( I_h \) is ramped from 1 \( \mu A \) to about 8.9 \( \mu A \) while \( I_s \) is a constant 1 \( \mu A \). \( V_h \) and \( V_s \) are measured and after subtraction of the offset voltage, are used to calculate the change in the resistances. When \( \alpha \) is known, \( \Delta T_h \) and \( \Delta T_s \) can then be determined. At the same time, the power is calculated using Eq. 52. The temperature changes are then plotted as a function of the power and a linear fit is made with the least-squares method in order to extract the slopes \( \frac{d\Delta T_h}{dP} \) and \( \frac{d\Delta T_s}{dP} \). A typical example of such a plot is shown in Fig. 20.

![Figure 20: Typical measurement result of the change in temperatures as a function of the applied power.](image)

The conductance of the wire can be calculated from Eqs. 44-45 or Eqs. 47-49 as these can be expressed as a function of the slopes. This becomes apparent when considering that

\[
\frac{d\Delta T_h}{dP} = \frac{\Delta T_h}{Q_h + Q_L}
\]

and likewise for \( \Delta T_s \).

4.3.4 Calculation of the conductivity

In order to determine the conductivity of the wire, a scanning electron microscope (SEM) is used to measure \( L \), the length that is bridging the gap between the membranes, as well as the width of the wire at both ends. The wurtzite nanowires that are used are expected to be hexagonal, but in most cases this can not be confirmed with SEM and neither can the orientation of the wire, see Fig. 21A. This means that the measured width could correspond to the edge-to-edge width, the corner-to-corner width or some width in between these limits.
The area of a hexagon, such as in Fig. 21B, can be calculated as either

\[ A = \frac{3}{2\sqrt{3}} w_1^2 \]  

(54)

or

\[ A = \frac{3}{8} \sqrt{3} w_2^2. \]  

(55)

There is a factor of \(3/4\) difference between the prefactors in these formulas, so using the wrong one would introduce a significant systematic error. In this project, neither of these formulas are used and instead the cross-section of the nanowires is assumed to be circular. In that case, \(A = \pi/D^2\) with \(D\) the measured diameter. Numerically, the value of \(\pi/4\) is between that of the prefactors in the formulas for the area of a hexagon. The error introduced this way is about 10-20%.

For very thick, micrometer scale wires, it is possible to see the hexagonal shape and orientation of the wire, as in Fig. 21C, and Eq. 55 can be used for the area. However, the hexagonal shape of these wire is not perfect as the facets are not equally large. As can be seen in the image, the width \(w_2\) is about 1.5 \(\mu m\) while the width of the top facet is less than half of that. It is likely that the thin wires have a similar imperfect shape as the thick ones.

If the diameter of the wire is constant, the conductivity can be simply determined from:

\[ \kappa = \frac{G_s L}{A}. \]  

(56)

Usually, the diameter of the wire is not constant. Assuming steady state heat conduction in a one-dimensional system with no internal heat generation, Fourier’s law can be used to derive the conductivity [46].

\[ Q_x = -\kappa A \frac{dT}{dx}. \]  

(57)

The heat flow through the wire, \(Q_x\), is constant and the diameter is assumed to change linearly as \(D = ax\), with the x-axis defined along the wire. \(A\) is the cross-sectional area of the wire, such that \(A = \pi a^2 x^2/4\). Then:

\[ \frac{4Q_x dx}{\pi a^2 x^2} = -\kappa dT. \]  

(58)

Integrating from \(x_1\) to \(x_2\), the positions where the wire touches the membranes, gives:

\[ \frac{4Q_x x^2}{\pi a^2} \int_{x_1}^{x_2} dx = -\kappa \int_{T_s}^{T_h} dT, \]  

(59)
and thus:

\[ \frac{4Q_x}{\pi a^2} \left( -\frac{1}{x_2} + \frac{1}{x_1} \right) = -\kappa(T_h - T_s). \]  \hspace{1cm} (60)

Considering that

\[ G_s = \frac{Q_x}{T_h - T_s}, \]  \hspace{1cm} (61)

\(\kappa\) can be found as:

\[ \kappa = \frac{4G_s}{\pi a^2} \left( \frac{1}{x_2} - \frac{1}{x_1} \right) = \frac{4G_s}{\pi} \frac{L}{D_1D_2}, \]  \hspace{1cm} (62)

with \(L = x_2 - x_1\) and \(D_{1/2}\) the diameter at either end of the wire.

For some wires, less than 10\% of all, there is a sudden step in the diameter. In those cases, the length between one membrane and the step has to be measured as well as the diameter at the edge of the membrane and right before the step. This \(L/(D_1D_2)\) then has to be summed with that calculated from the length between the step and the other membrane and relevant diameters.

### 4.3.5 Electrical conductivity

Measuring the electrical conductivity is very simple. If there is contact to the wire through all four contacts, a four-point measurement can be done, eliminating the line and contact resistance. This is in practice never the case however. Electrical measurements are therefore done in a two-point configuration.

For this, a voltage is applied between the two contacts and a current is measured. The voltage is swept from -20 to 20 mV. The resistance is then extracted from a linear fit through a plot of voltage versus current. This process can be repeated at different temperatures.

The measured resistance is the sum of line, contact and wire resistance, but only the wire resistance is of interest. It is not possible to measure any of these independently, but it is possible to make an estimation of the line resistance. This can be done by measuring the resistance of other platinum lines on the same device (those leading to the coil), which are designed to be identical and should have similar resistances. In that way, an approximate value for the wire and contact resistance can be obtained.

The conductance is of course just the inverse of the resistance and the conductivity can be calculated from it in the same way as the thermal conductivity from the thermal conductance. Doing this only makes sense if only the conductance of the wire is used however, so the contact resistance has to be very small for this to have any validity.
4.4 Measurement sensitivity

The minimum thermal conductance that can be measured with this setup is determined by the sensitivity. This noise-equivalent sample conductance, $NEG_s$, is proportional to the noise-equivalent temperature increase of the sensing membrane, $NET$, according to:

$$NEG_s = G_{bs} \frac{NET}{\Delta T_h - \Delta T_s},$$

as in Eq. (45). The noise in the temperature is in turn set by the noise in the resistance measurement, $NER$:

$$NET = \frac{1}{\alpha} \frac{NER}{R_s}.$$

The noise-equivalent resistance can be estimated from a measurement of the resistance with no applied heating, so that $NER/R_s \approx 2.5 \cdot 10^{-4}$. Typical values for $\alpha$ are between 1.1 and $1.8 \cdot 10^{-3}$. This places the $NET$ between 0.13 and 0.23 K. This noise arises from the inherent limitations of the measurement equipment. The dominant source of noise is in the current source.

The measured beam conductance usually has a value between 33 and 47 nW·K$^{-1}$. The difference between $\Delta T_h$ and $\Delta T_s$ depends on the actual conductance of the wire and is naturally smaller for larger wire conductance. For a very small wire conductance, it is usually as large as 40 K.

The noise-equivalent conductance then becomes about 0.3 nW·K$^{-1}$. Any conductance smaller than this value can not be measured with the device and setup as they are. Conductances that are larger than 0.3 nW·K$^{-1}$, but still close to it, will also be difficult to measure as they are significantly affected by noise.
4.5 Sources of measurement error

There are several mechanisms which may cause systematic errors in these measurements. First of all there is the possibility that the heat that is conducted from one membrane to the other not only goes through the wire. Heat transfer can also occur through radiation or conduction through air. The thermal conductance through radiation can be estimated as:

\[ G_{\text{rad}} = \sigma \epsilon (T_s + T_h) (T_s^2 + T_h^2) F_{h-s} A, \] (65)

where \( \sigma \approx 5.67 \times 10^{-8} \text{W} \cdot \text{m}^{-2} \text{K}^{-4} \) is the Stefan–Boltzmann constant, \( F_{h-s} \) is the view factor between the two membranes, \( A \) the area of a membrane that is facing toward the other membrane \[42\] and \( \epsilon \) the emissivity. \( F_{h-s} \) can be calculated (see appendix \[C.2\]) and is approximately 0.038 in this configuration, while the area of one membrane is about 9 \( \mu \text{m}^2 \). The emissivity is assumed equal to one.

The effect of the beams is more difficult to include, as these do not have a constant temperature. Their area is much larger than that of the membranes, as they are much longer. However, the fraction of the heat from the beams on the side of the heating membrane that will actually heat up the sensing membrane, is very small. Therefore, this effect is not taken into account in the calculations.

When measuring at room temperature, typical values for \( T_h \) and \( T_s \) are 330 and 300 K, so that \( G_{\text{rad}} = 2.4 \times 10^{-3} \text{nW} \cdot \text{K}^{-1} \). The maximum temperatures reached during any experiment are about 400 and 380 K for \( T_h \) and \( T_s \) respectively and \( G_{\text{rad}} = 4.6 \times 10^{-3} \text{nW} \cdot \text{K}^{-1} \). Both these values are well below the measurement sensitivity 0.3 nW \cdot K\(^{-1}\). Considering that the emissivity is likely to be less than one, \( G_{\text{rad}} \) will actually be even lower than calculated.

Conduction through air can be minimized by measuring under vacuum conditions. During most measurements, this is done with a pressure of about \( 5 \times 10^{-6} \text{mbar} \). At this pressure, the mean free path of air molecules is of the order of 10 meter, which is much larger than the distance between the membranes, \( d \). Kinetic theory then applies, such that:

\[ \kappa_{\text{air}} = \frac{C v d}{3}, \] (66)

and

\[ G_{\text{air}} = \frac{C v A}{3}, \] (67)

with \( C \) and \( v \) the heat capacity and velocity of air molecules \[42\]. This equation is likely to grossly overestimate the conduction, as a molecule that originates from one membrane has only a small chance to hit the other membrane. The calculated conduction is \( G_{\text{air}} = 2.6 \times 10^{-3} \text{nW} \cdot \text{K}^{-1} \). Again well below the measurement sensitivity.

The influence of radiation and conduction through air is not only something to consider between the two membranes, but also between the heated membrane and the environment. If these effects are significant, they can negatively impact the measurement sensitivity. This conductance is measured along with the beam conductance, but it is good to calculate it as well. It obviously also exists from the sensing membrane to the environment, but since the temperature of the sensing membrane is not much larger than the system temperature, this is neglected.

The effect of radiation heat loss to the etched substrate can be calculated using Eq. \[65\] with the area of the membrane being 400 \( \mu \text{m}^2 \). The view factor can not be calculated exactly in this configuration, but it is likely close to one. The system temperature is between room temperature and 360 K, while the temperature of the hot membrane is up to 40 K higher. So at the maximum temperature, the radiation conductance to the substrate becomes 4.4 nW \cdot K\(^{-1}\). This is small compared to the calculated beam conductance of 127 nW \cdot K\(^{-1}\).

Conduction through air to the substrate can be calculated from Eq. \[67\] using the area of the whole membrane of about 400 \( \mu \text{m}^2 \). The air conductance to the substrate is then 0.11 nW \cdot K\(^{-1}\). This means that all sources of heat transfer from the membrane to the environment should amount to about 131.5 nW \cdot K\(^{-1}\).
Some additional errors may be introduced if the implicit assumptions made in the derivations of Sec. 4.3 are not entirely justified. This includes the possibilities that the temperature of each membrane is not uniform; that the temperature profile of the SiN beams is not linear, which could happen if radiation is nonnegligible, or that the large temperature excursion of the heating membrane causes temperature dependent properties of the system to change [47]. None of these mechanisms are however expected to cause significant problems.

A potentially large source of error is the thermal contact resistance. As discussed in Sec. 4.1.3, platinum can be deposited in order to improve thermal contacts. This is often done in other work before measuring the thermal conductivity. In this project, measurements are done before and after EBID and an analysis is made of whether it is really necessary. As the contact area between a wire and membrane or Pt deposit is proportional to the wire diameter, but the thermal conductance is proportional to the diameter squared, it is expected that contact resistance will be less of a problem for thinner wires.

The largest source of error is likely the measurement of the temperature coefficient of resistance, \( \alpha \). Any error in \( \alpha \) will also cause an error in the temperature measurement for that membrane. When determining \( \alpha \) as described in Sec. 4.3.1, there is an error due to noise of about 5% in the slope \( dR/dT \) and negligible error in \( R \). As a result, the measured temperature has an error of about 5%. As there are errors in both \( T_h \) and \( T_s \), the error in \( G_s \) can then be as large as 15–20%.

Noise in the temperature measurement also introduces some errors during the conductance experiment. This random error of about 0.1–0.2 K for each data point has little effect on the overall result however, as each measurement has at least 200 data points. When fitting the slopes of \( \Delta T_h \) and \( \Delta T_s \) as a function of the power, this error propagates into an error in the slopes. The conductance that is calculated from those slopes then has an error due to noise of about 2%. Compared to other error sources, this is quite small.

As discussed in Sec. 4.3.4, there is also an error when calculating the conductivity due to the uncertain shape and orientation of the wire. The size of this error is unknown, and different for every wire. Together with the error in the conductance, this means that conductivities measured in this work may deviate up to 30 or 40% from their correct values if there is no additional systematic error, such as a contact resistance. A large contact resistance could cause the measured values to be much too low.
5 Results and discussion

The final results of the measurements are discussed in this chapter. The first section, 5.1, describes a problem that was encountered while measuring, namely the asymmetry of the devices. This is then corrected for in the interpretation of the remaining experiments. Measurements of the thermal conductivity of wires with 40-250 nm diameters are shown in Sec. 5.2 and those of 700-1500 nm diameters in Sec. 5.3. A qualitative model that can help the understanding of the data is described in Sec. 5.4 and finally some electrical measurements are shown in Sec. 5.5.

5.1 Asymmetry of the devices

For each wire, measurements are done at system temperatures between room temperature and 360 K. For each temperature, two measurements are done. First, one membrane is used as heating membrane and the other as sensing membrane, then their roles are exchanged. Initially, the conductances are calculated using the simpler approach of Eq. 44 and Eq. 45, which assumes equal beam conductances for both membranes. It should not matter for the thermal conductance which side is used as heater, yet there are significant differences between the two sides in many measurements. One such measurement is shown in Fig. 22 for a nanowire from growth series 2285.

![Figure 22: Example of the effect of asymmetry on a measurement. Left: SEM image of a device. The two membranes are labeled 1 and 2 in order to distinguish between them. Right: results of a series of measurements of this device. The black data corresponds to heating of side 1 and the blue data to heating of side 2.](image)

There has been some work showing direction dependent thermal conductivity in asymmetrical systems [48, 49], an effect referred to as thermal rectification. In those cases, a larger part of the mass was concentrated on one side of the system, as in the case of a tapered nanowire. However, the asymmetry in those systems is far larger than in any of the wires used in this project and the rectification effect is only a few percent. This effect is defined as:

\[
\text{Rectification} = \frac{\kappa_{1\rightarrow2} - \kappa_{2\rightarrow1}}{\kappa_{2\rightarrow1}} \cdot 100\%.
\]

In the example of Fig. 22, the rectification is as large as 20-30%. This wire has diameters of about 72 and 75 nm on either side, and a length of 3.86 µm in between, giving a degree of tapering of only 0.016°. An effect of thermal rectification can therefore certainly not explain these results.

It is also possible that thermal contact resistance has an effect on the measured asymmetry. On its own, a contact resistance that is different on either side will not lead to the measurement of different thermal conductivities. However, considering that the contact resistance may decrease with increasing
temperature, there could be an effect. As the temperature is increased, a contact resistance that is larger to begin with is likely to decrease more than a resistance that was already small. Since the temperature of the heating membrane increases more than that of the sensing membrane, this can lead to asymmetry in the measurements. It will not be a large effect though, as the difference between $\Delta T_h$ and $\Delta T_s$ is typically only a few tens of kelvin. Thus, this effect can not explain the results of Fig. 22.

Similarly, a temperature dependence of the conductivity combined with tapering of the nanowire could also lead to asymmetry. In that case, there is a difference depending on whether the thicker or the thinner side of the wire is heated. If the thicker, more conducting part is heated, the overall measured conductivity will be lower than if the thinner part is heated. However, there does not seem to be any temperature dependence in the measured range and the wire in Fig. 22 is barely tapered at all. This also does not explain the results.

Instead, the approach of Eqs. 47 and 49 is used to determine an asymmetry in the beam conductances of the two membranes. For the example device, this gives an average ratio $G_{b1}/G_{b2}=1.14$, which is not an unreasonable level of asymmetry considering the accuracy of fabrication processes. Contrary to other explanations, asymmetry of the device can thus account for a large asymmetry in the measurements. If it is assumed that the conductivity of the nanowire is the same in both directions, neglecting the previously mentioned effects, then the device asymmetry can be corrected for. The result of this correction for the example data in this section is shown in Fig. 23.

![Figure 23: Measurement data on the same device as in Fig. 22 but now corrected for the device asymmetry.](image)

So far, only a single device has been discussed. Asymmetry is an effect that happens to some extent in all devices however. Therefore, $G_{b1}/G_{b2}$ has been calculated for every new device and the correction was applied to all measurements. A histogram of different values of $G_{b1}/G_{b2}$ is shown in Fig. 24. For many devices, it is very close to one and the asymmetry does not cause significant problems. The devices that do have a ratio far from 1 coincide with those devices that show a large difference between the two directions if the correction is not applied.
It is good to verify the numbers for $G_{b1}/G_{b2}$ by measuring $G_{b1}$ and $G_{b2}$ independently. This can be done on devices that have no wires on them, and thus no conductance between the two membranes. For those devices $\Delta T_s \approx 0$ and:

$$G_b \approx \frac{1}{d \Delta T_h / d P}$$

(69)

The beam conductances measured this way are between 33 and 47 nW·K$^{-1}$ and the ratios are between 0.87 and 1.03 for seven different devices. This is in agreement with the ratios in Fig. 24 suggesting that this approach is indeed valid. All other measurements of the thermal conductivity that are shown in this thesis therefore include the correction for the asymmetry.

Although not directly related to the asymmetry, it is also worth noting that the measured beam conductances are a factor of 3 or 4 smaller than the value of 127 nW·K$^{-1}$ that was calculated based on the designed geometry of the beams (see Sec. 4.1). This shows that geometry of the beams can be quite different from what is expected. Most likely the SiN$_x$ beams are thinner than expected. This may have happened during the underetching process. This makes the devices actually better than designed.
5.2 Thermal measurements on nanowires

5.2.1 Temperature dependence

Measurements of the thermal conductivity of InAs nanowires with diameters between 40 and 240 nm have been performed in order to determine the dependence of $\kappa$ on the diameter. Nanowires from four different growth series are used, and some of these are etched in order to reach smaller sizes. Every wire is measured at system temperatures between room temperature and 360 K. The data from one wire of growth series 2151 is shown in Fig. 25 as an example. This wire has diameters 106 and 199 nm at each end, and a length of 4.85 µm in between.

Figure 25: Example of a series of measurements. A) SEM image of the device on which these measurements are done. B) The change of temperature as a function of the power, from which the conductance is extracted. In this case, the system is at room temperature. C) The full series of measurements for this wire.

It can be seen in Fig. 25B that the temperature increases linearly with the applied power, as expected. This shows that the assumption of linearity is indeed valid and that nothing went wrong in this measurement. Any problem that can occur while measuring, such as large resistance changes due to unstable tips, would be apparent from this graph. Plots like this are made for every measurement and serve not only to extract the slopes needed for the calculations, but also to detect any errors early on.

The main point of Fig. 25C is to show the absence of any temperature dependence in this range. Within the error bars, the thermal conductivity is entirely constant. However, it should be noted that the temperature on the x-axis is the system temperature. The actual temperature of the wire during the measurement is always higher. This means that the conductivity is never measured at one specific temperature, but over a range of temperatures. The average of $T_h$ and $T_s$ is up to 20 K larger than the system temperature, so Fig. 25C is a progressing average.

The absence of a temperature dependence is not only there for this particular measurement, but can be seen for every device and every wire. Because of this, it is justified to take the average of these eight data points in order to find a single value of $\kappa$ that can be compared to that for other wires. A value for comparison could also be taken at a specific temperature, but the random variations between data points in graphs such as this one mean that no single temperature will show the correct behavior. In Fig. 25C for example, there are differences larger than 0.2 W·m$^{-1}$K$^{-1}$ between the data points, while in other graphs these random differences are often even larger. Therefore it is better to take the average.

The error bars in Fig. 25C are determined by the errors that arise from the least square fits of temperature as a function of power, which are very small, and also from the SEM measurements of the length and diameter of the nanowire. When calculating a single value of $\kappa$ for a wire, the average and standard deviation of the conductance are used. From those, the conductivity and its error are determined. For this example, this gives $\kappa=4.2\pm0.3$ W·m$^{-1}$K$^{-1}$. 
5.2.2 Diameter dependence

An overview of the results of the measured conductivities as a function of the wire diameter is shown in Fig. 26.

![Figure 26: The measured average thermal conductivity as a function of the diameter of the nanowire.](image)

It appears from this graph that any diameter dependence is smaller than the scatter between the data points. However, there is a considerable reduction compared to bulk, as $\kappa_{\text{bulk}} = 27 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$ and taking the average from this graph gives $\kappa = 3.9 \pm 1.0 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$.

This value is quite similar to what has been found experimentally or predicted theoretically in other studies, such as those described in Sec. 3.4. The reduction from bulk can be explained with increased boundary scattering, but a stronger diameter dependence is typically expected. The calculations of Mingo predict that $\kappa$ should increase from about 3 to 8 W·m⁻¹·K⁻¹ in this range, but this is not observed. This theory contains assumptions about for example the specularity of the wires though. Therefore, it is possible that the diameter dependence is weaker than predicted.

A positive aspect of this data is the reproducibility over a large number of measurements. Despite the large potential errors, there are few measurements that deviate strongly from the others. The values of the thermal conductivity are also very similar across different growth series. The differences between specific data points in Fig. 26 can be accounted for by the 30–40% errors that are inherent to the method. It is possible that the structural aspects of individual wires, such as the density of defects or the condition of its surface, also affect the measured $\kappa$, but the scatter between the measurements is too large to say so conclusively.

5.2.3 Contact resistance

In order to verify that the nanowires have good thermal contact, a layer of platinum is deposited on sections of several nanowires that are lying on devices. This should ensure good thermal contact in those cases. SEM images of these Pt deposits are shown in Fig. 27.
A total of five devices with nanowires has received a Pt deposition and the thermal conductivity has been measured for each of these wires before and after the EBID. For some of these wires, the thermal conductivity was already in line with that of similar wires beforehand, while for other wires it was unusually low. In one case, there appeared to be no thermal contact at all as no signal beyond the noise level could be measured. An overview of the results is shown in Fig. 28 and the measurement series of two specific devices are shown in Fig. 29.

Figure 28: Overview of the measurements that were changed due to EBID. The filled circles are before the EBID, and the open squares after. Every color corresponds to a single wire.
As can be seen in the graphs, EBID can increase the conductance, especially when it is anomalously low to begin with. It is, however, often not needed to use EBID. The EBID process does not increase the conductance to beyond the level of most measurements, indicating that the contact was already good during those measurements. For wires that had no contact or bad contact to begin with, such as for example the wire behind the data in Fig. 29A, EBID does cause a significant improvement. This is a small minority of the wires however.

In two cases, the EBID process actually decreased the conductance. This is unexpected, as there is no way that the thermal contact could become worse after depositing Pt. Instead, this effect is probably due to the wire being damaged by the deposition process. In some cases, there is visible damage, such as in Fig. 27B. Damage of this type would either reduce the conductance to zero, or hardly affect it at all, depending on where along the wire it takes place. But if a nanowire can be damaged in this way, it seems probable that additional, invisible damage occurs. Fig. 29B shows the data for a wire that had a decreased thermal conductivity after EBID.

There are also changes to the diameters of the nanowires after the deposition process, as can be seen in Fig. 28. These changes can be either positive or negative. A positive change might be due to some Pt being deposited outside the designated area, but a negative change points to damage being caused to the wire. In either case, the uncertainty in the measurements is increased as diameter profile of the nanowire is no longer linear.

5.2.4 Length dependence

In some cases, it is possible for the thermal conductivity of nanowires to depend on the length. For example, in the case of (quasi-)ballistic transport, $\kappa$ can decrease with decreasing length. This was recently observed in SiGe nanowires over a large length of more than 8 $\mu$m [51] and also in graphene [52]. The reasons for this process are not well understood, but it is nevertheless good to verify whether this is the case in this study as well. Therefore, the measured thermal conductivity is shown in Fig. 30 as a function of the suspended length between the membranes.
Figure 30: The measured thermal conductivity of InAs nanowires as a function of the length.

As can be seen, any length dependence of $\kappa$ is obscured by the scatter between measurements. The absence of a length dependence can indicate diffusive thermal transport.

Length dependence could also arise due to thermal contact resistance. This is a different effect as what was observed by others, but it can potentially cause a length dependence. This is because the calculation of $\kappa$ includes the length, while the contact resistance is not affected by the length at all. The total conductance in that case is:

$$\frac{1}{G_{\text{total}}} = \frac{1}{G_{\text{wire}}} + \frac{1}{G_{\text{contact}}},$$

with $G_{\text{wire}} \propto L^{-1}$ and $G_{\text{contact}}$ independent of length. Considering that $\kappa$ is taken to be proportional to $G_{\text{total}}L$, it can be derived that $\kappa$ should depend on the length as follows:

$$\kappa \propto \frac{L}{C + L},$$

with $C$ a constant that describes the size of the contact conductance relative to that of the actual wire. $C = 0$ describes the ideal case where there is no contact resistance at all and $C = \infty$ means the wire is not touching one of the membranes. Of course, the contact resistance is going to be different for each wire, so this equation can not be applied as a fit to the data. The fact that there is no visible length dependence in Fig. 30 does however strengthen the presumption that the contact resistance is consistently low.
5.3 Thermal measurements on microwires

A number of measurements was done on microwires (growth 2184, see appendix A) as well. From these wires, it is expected that they exhibit bulk-like behavior and thus have a thermal conductivity close to 27 W·m⁻¹K⁻¹. This is not what is measured however. Both before and after depositing Pt, the conductivity is far lower than bulk. These results are shown in Fig. 31.

![Thermal conductivity measurements for microwires](image)

**Figure 31:** Thermal conductivity measurements for microwires. Solid circles correspond to measurements without Pt deposits, open squares to measurements after one Pt deposit and triangles after two. Every color corresponds to a single wire.

Measurements were done on several wires with and without platinum. As the deposition process sometimes goes wrong and wires fall off the devices, it is not always possible to measure a single wire before and after deposition. In those cases, the wires had to be quickly replaced and there was no time to measure the conductivity before deposition. There were also several measurements on microwires that gave no signal above the noise level. These are not included in Fig. 31.

In any case, the measured conductivities are not only much lower than the bulk value, but are in fact lower than those of the much thinner nanowires. This disagrees with any predictions about the diameter dependence of the conductivity. There is no reason why the thermal conductivity of these microwires should be intrinsically low. The growth of these wires is similar to that of the other wires, just longer, so it is not expected that the crystal quality is much lower. The hexagonal shape of these wires can be clearly seen with SEM, and indicates that these wires are wurtzite and certainly not amorphous. However, one measurement gives a $\kappa$ smaller than 0.5 W·m⁻¹K⁻¹, which is below the amorphous limit. Because of this, the measured values must be related to some problem with the measurements.

A possible problem might be the temperature measurement. If the conductance of the wire is very large, it could be that the temperature of the heating membrane is not uniform. The temperature of the wire on the membrane will then be lower than what is measured with the coil. As the conductance of the beams supporting the membranes is measured, it is possible to make a fair estimate of the conductance of the membrane itself as well. When combining this information with the knowledge of how much heat is produced in the system, it becomes clear that there can never be significant temperature differences.
5.3.1 Contact resistance

The reason for this anomalously small conductance is the contact resistance. Despite having a larger contact area than the small wires, the microwires have a much larger contact resistance. Many of these wires do not even produce any signal above the noise level, even though they are clearly lying on a device. This is likely related to the stiffness of these thick wires. While thin wires may bend and accommodate to the device, thick wires remain rigid and can therefore lie on one membrane without touching the other.

The microwires that do make contact to both membranes show a conductance much larger than the nanowires, but the conductivity is calculated to be small due to their large diameter. Regardless of whether the wire made contact to begin with, EBID of Pt can improve the contact. In some cases however, the wires actually fall off the devices before the deposition can start. This is likely to happen only when the contact is bad and the wire does not adhere strongly to the device. EBID on microwires necessarily also requires much larger amounts of Pt and it is not always clearly visible whether contact has been established. Therefore, when doing EBID on very thick wires, a high deposition is first made next to the wire and then a layer of Pt is deposited on the wire and the earlier pile of Pt to ensure contact. Some SEM images are shown in Fig. 32.

![Figure 32: Tilted SEM images of Pt depositions on microwires. These images correspond to the black data points in Fig. 31](image)

A) Made after the first Pt deposition. There clearly was a layer of Pt deposited, but it did not make contact between the wire and the device. B) Made after the second deposition. Now the wire does make contact to the device through a pile of Pt on one side of it.

One wire that was measured after Pt deposition received another deposition of Pt adjacent to the first one, see Fig. 33A-B. In this way, the contact made by EBID roughly doubled in size. After the second deposition, the thermal conductivity increased further (see Fig. 33C'), showing that the thermal contact could be further improved. Only when the conductance does not increase any more with a larger contact size can the contact be considered good. Considering the extent to which one or two depositions increased the conductance, it seems unrealistic that contact resistance can be eliminated from this system. Therefore, near-bulk values of the thermal conductivity of InAs microwires can not be measured in this system.
Figure 33: A) SEM image of a microwire after one Pt deposition. This wire was already dirty before the deposition process. B) The same wire after two depositions. C) Comparison of the thermal conductivity of this wire after one and two Pt depositions.

Assuming that the microwires should have a conductivity comparable to bulk, it is possible to derive the magnitude of the contact resistance. This can be done simply by considering what resistance should have been measured if there had been no problem with the contacts, and subtracting this from the actually measured resistance. Since this assumed bulk wire resistance is typically an order of magnitude smaller than the measured resistance, the subtraction is only a small correction.

The contact area can subsequently be estimated from SEM images. Any wires that only have contact between the wire and the membrane and no EBID Pt contacts are not considered, as the area can not be quantified. Often wires that appear to be in contact with the membrane turn out not to be, so it can not be seen if and where such a contact does exist. The contact resistance is plotted as a function of contact area in Fig. 34.

Figure 34: Contact resistance calculated under the assumption of bulk InAs conductivity (27 W·m⁻¹K⁻¹) for the wire, as a function of the area of the contacts estimated from SEM images. Every color corresponds to a single wire.
From this graph, the resistance appears to decrease with increasing contact area, although the scatter is large and there are too few data points to observe a real trend in them. It can only be said that it likely would require significantly larger contacts to reduce the contact resistance to acceptable levels.

The values of the contact resistance are quite large, of the order of $10^6$ K·W$^{-1}$. This is much larger than what could be calculated with the AMM or DMM following Eqs. 30 or 32. From the DMM, with $\alpha_{Pt\rightarrow InAs} \approx 0.55$ (see App. [5] for the values of the constants used in this calculation), contact resistances of only a few hundred K·W$^{-1}$ are calculated. This is several orders of magnitude smaller than what was measured. In other work, a calculated contact resistance to an InAs wire also turned out much lower than the measurement [28]. In that case, it could be explained by the bonding to the interface not being as strong as the model assumes. This is likely to be true in this project as well for the microwires that did not receive additional Pt contacts. As mentioned before, these wires some times fall off the devices, so they are clearly not bonded strongly to the surface.

The bonding of a platinum deposition to the wire is likely to be stronger, but these depositions are also very dirty. They are not pure platinum, but instead consist mostly of carbon with only about 16% Pt. This means that the interface is not the clean Pt-InAs interface that the DMM model assumes. It is then not surprising that the measured resistance is much higher than the calculated resistance.

It is possible that the conductance is limited by the conduction through the deposited material. The Pt has a conductivity of about 70 W·m$^{-1}$K$^{-1}$, while the carbon typically has a very low conductivity of maybe 1 W·m$^{-1}$K$^{-1}$ [53]. The area where the deposition is in touch with the Pt line is about 0.25 $\mu$m$^2$ and the height is comparable to the diameter of the wire. Based on these numbers, an order of magnitude estimation of the conductance of the Pt deposition can be made. This conductance is of the same order as that of a bulk-like wire, and thus can not explain the high resistance.

The most likely explanation for these results is actually the large diameter of the wires. The conductance of the wire scales with the diameter squared, but the contact conductance only scales linearly with the diameter. This means that for larger diameters, the system is more and more dominated by the contact resistance.
5.4 Qualitative model

The thermal conductivity of a nanowire is modeled as having an exponential dependence on the diameter. This has been done in other work as well, and has been shown to describe experimental data for some other materials reasonably well [54]. The phonon mean free path, $l_0$, is also included in the model and determines how strongly the system is affected by surface scattering. Thus:

$$\kappa \propto \exp \left( -\frac{l_0}{d} \right)_0,$$

with $d$ the diameter of the wire.

In order to explain the results of this work, this model is adapted to include contact resistance. Consider that the real conductance of the wire is proportional to the conductivity times the square of the diameter, while the contact conductance is linearly proportional to the diameter. The total conductance is:

$$\frac{1}{G_{\text{total}}} = \frac{1}{G_{\text{wire}}} + \frac{1}{G_{\text{contact}}} = \frac{C_1 d^2}{C_1 \kappa d + C_2 d},$$

with $G_{\text{wire}} = C_1 \kappa d^2$ and $G_{\text{contact}} = C_2 d$. Then:

$$G_{\text{total}} = \frac{C_1 C_2 \kappa d^2}{C_1 \kappa d + C_2}.$$

The new equation for the calculated thermal conductivity, $\kappa_{\text{calc}}$, then becomes:

$$\kappa_{\text{calc}} = \frac{G_{\text{total}} L}{d^2} = \frac{C_1 C_2 L}{C_2 \exp \left( \frac{l_0}{d} \right) + C_3 d}.$$

This expression can be simplified by collecting all the unknown constants into a single constant, $C_3$, that describes the relative strength of the boundary resistance compared to the wire resistance:

$$\kappa_{\text{calc}} \propto \frac{1}{\exp \left( \frac{l_0}{d} \right) + C_3 d}.$$

This equation was plotted in Fig. 35 for several different values of $C_3$, in order to see the effect of a stronger contact resistance.
For large enough $C_3$, the model reproduces the trend of decreasing $\kappa$ for large diameters. This shows that the unexpectedly small conductances measured for very thick wires can indeed be explained by the linear dependence of the contact conductance on the wire diameter.

The model makes no quantitative predictions, as the right value for all of the constants is not known a priori, but it can be used to fit to the data. However, the quality of the contact is obviously not the same for every wire, so there is no one value for $C_3$. This means that any $C_3$ extracted from this fit is only an average over all the measurements. The result is shown in Fig. 36 in order to demonstrate that indeed the qualitative behavior is reproduced.
Figure 36: Fit of the model to the data. Those data points that were taken from wires with platinum depositions were not included, as in those cases the relative strength of the boundary resistance compared to the wire resistance will be significantly different. The values of $l_0$ and $C_3$ are 115.5 nm and $39.5 \mu m^{-1}$, respectively.

As mentioned before, the model is not meant to accurately explain all the measurements, but only to reproduce the qualitative behavior for large diameters. For small diameters, the model is not expected to fit well to the data. A more realistic model would have to account for the fact that the quality of the contact as well as the phonon mean free path are not likely to be the same for every wire.
5.5 Electrical measurements

In nearly all cases, a wire placed on a device will not make electrical contact to the Pt lines on the device, even after EBID platinum deposition. There were two exceptions in this study, both microwires with EBID contacts. For these two, the electrical resistance was measured at different temperatures. Since the measurements were done with only two points, the measured resistance does unfortunately include contributions from the lines and contacts. The former is corrected for by measuring the resistance of other lines, designed to be identical, at different temperatures and subtracting those values. The results are then shown in Fig. 37.

Figure 37: A) Measured resistance of two microwires (blue and black), including contact resistance. B) Logarithm of the resistance versus the inverse temperature. For an intrinsic semiconductor, this should be linear.

The resistance values of the two wires are very different. Their diameters are 720-750 nm (black line) and 715-910 nm (blue line), while their lengths are 5.738 µm and 5.487 µm respectively. These geometrical differences are much too small to explain the large differences in resistance. If they are used to calculate a resistivity, the difference is still large. It is likely that the one with the larger resistance has a much larger contribution from the contacts to that resistance.

The resistivity of a semiconductor is expected to decrease as Eq. 33. That equation can be rewritten to state that the natural logarithm of the resistivity should be linearly proportional to $T^{-1}$, with slope $E_g/2k_b$. This can be used to extract the bandgap of the semiconductor. A plot of $\log \rho/\rho_0$ against $T^{-1}$ is shown in Fig. 37B. This is plot is not as nicely linear as would be expected of a purely semiconducting system, which indicates that contact resistance plays a significant role here. If a linear fit is made anyway, then the $E_g$ extracted from the two measurements differs significantly from what is reported in literature.

The presence of a significant electrical contact resistance is consistent with the large thermal resistance that was also observed. It appears that contact resistance is a problem that affects every aspect of thermoelectric measurements on microwires.
6 Conclusions and outlook

6.1 Conclusions

The results of this work lead to two main conclusions, for nanowires and for microwires.

The thermal conductivity measurements on nanowires are reliable. The results agree quite well with those that were found in other studies, both theoretical and experimental. As an enhancement of the contacts through platinum deposition did not increase the measured conductivity beyond the level of the other measurements, it has also been shown that the thermal contact is already good in most cases. This was further confirmed by the absence of any length dependence of the thermal conductivity.

Within the measured range of nanowire diameters, any diameter dependence of the thermal conductivity was hidden by the scatter between data points. Theoretical calculations predicted a variation of the thermal conductivity between 3 and 8 $W\cdot m^{-1}K^{-1}$ in this range of diameters, but this was not observed. It is possible that this theory overestimates the strength of the diameter dependence however. A weaker dependence could certainly be present in the data, but be obscured by the scatter.

For microwires, the measurement method is less effective. Contact resistance causes the thermal conductance to be much lower than expected, and makes it impossible to determine the actual conductivity of the microwires. The model shows that this problem will only get worse with thicker wires. Additionally, even for electrical measurements after platinum deposition, the contacts significantly increase the resistance.

Across all measurements, three things were shown that may be relevant for future measurements with similar devices. That is: asymmetry of the devices can affect the results, platinum deposition is often not needed for measurements on nanowires and measurements on microwires are not possible.

6.2 Outlook

In the future, it will be good to measure thinner wires. Large effects are only predicted for small wires, so it will be interesting to see how the thermal conductivity develops below 40 nm diameter. To do this, it is important to reduce the level of noise in the measurements, as these thin wires will have very low conductances barely above the noise level. This could be done for example by using a Wheatstone bridge setup [55].

Additionally, the devices and methods will need to be improved so that also electrical properties and the Seebeck coefficient can be reliably measured. For example, by adapting the devices to have an additional platinum contact on top of the wires to hopefully cause good electrical contact. The setup will also need to be improved in order to measure the Seebeck coefficient, as this has so far proven to be difficult.

Once all thermoelectric properties of these InAs nanowires are measurable, it is time to move on to more interesting systems. InAs itself is not likely to lead to an application, it is merely a model system. However, measurements on InSb or various heterostructures can lead to applications and are therefore interesting to do in the future.
7 Acknowledgements

I would like to acknowledge the contributions to this project of Milo Swinkels, who fabricated the devices, developed the model and helped in other ways, and Alessandro Cavalli, who grew the InAs nanowires. Additionally, Ilaria Zardo, Douglas Oliveira, Erik Bakkers and Rob van der Heijden were involved in discussions, at times contributing valuable insights.
References


## A Properties of different nanowire growths

<table>
<thead>
<tr>
<th>Number</th>
<th>Diameter range (nm)</th>
<th>Typical tapering (°)</th>
<th>Average RMS roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1475</td>
<td>80–140</td>
<td>0.02–0.3</td>
<td>0.38</td>
</tr>
<tr>
<td>2072</td>
<td>25–300</td>
<td>0.3–0.9</td>
<td>0.58</td>
</tr>
<tr>
<td>2184</td>
<td>850–1500</td>
<td>0.15–0.3</td>
<td>0.35</td>
</tr>
<tr>
<td>2285</td>
<td>120–140</td>
<td>0.005–0.3</td>
<td>Unknown¹</td>
</tr>
<tr>
<td>2151</td>
<td>80–250</td>
<td>0.4–0.5</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table 1: Properties of different growths of nanowires used throughout this project.

<table>
<thead>
<tr>
<th>Number</th>
<th>Growth Temperature (°C)</th>
<th>Growth time (min)</th>
<th>Precursor flows (sccm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1475</td>
<td>480</td>
<td>InP: 4, InAs: 10</td>
<td>TMIn: 40, AsH₃: 60</td>
</tr>
<tr>
<td>2072</td>
<td>480</td>
<td>InP: 4, InAs: 10</td>
<td>TMIn: 40, AsH₃: 60</td>
</tr>
<tr>
<td>2184</td>
<td>540</td>
<td>InP: 1, InAs: 180</td>
<td>TMIn: 20, AsH₃: 7.5</td>
</tr>
<tr>
<td>2285</td>
<td>540</td>
<td>InP: 1, InAs: 18</td>
<td>TMIn: 8, AsH₃: 1</td>
</tr>
<tr>
<td>2151</td>
<td>480</td>
<td>InP: 4, InAs: 72</td>
<td>TMIn: 8, AsH₃: 7</td>
</tr>
</tbody>
</table>

Table 2: Growth conditions of different growths of nanowires used throughout this project.

¹But expected to be similar to the other measurements.
²Standard cubic centimeter per minute.
B Properties of used materials

B.1 Indium arsenide

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity</td>
<td>27 W·m⁻¹K⁻¹</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>4·10⁴ cm²V⁻¹s⁻¹</td>
</tr>
<tr>
<td>Energy gap</td>
<td>354 meV</td>
</tr>
<tr>
<td>Intrinsic carrier concentration</td>
<td>1·10¹⁵ cm⁻³</td>
</tr>
<tr>
<td>Intrinsic resistivity</td>
<td>0.16 Ω·cm</td>
</tr>
<tr>
<td>Mass density</td>
<td>5.68 g·cm⁻³</td>
</tr>
<tr>
<td>Effective electron mass</td>
<td>0.023 m₀</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>6.0583 Å</td>
</tr>
<tr>
<td>Debye temperature</td>
<td>280 K</td>
</tr>
<tr>
<td>Specific heat</td>
<td>0.25 J·g⁻¹K⁻¹</td>
</tr>
<tr>
<td>Sound velocity</td>
<td>5.5·10³ m·s⁻¹</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>1215 K</td>
</tr>
</tbody>
</table>

Table 3: Properties of bulk InAs, from the Ioffe Physico-Technical Institute unless otherwise specified.

B.2 Silicon nitride

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity</td>
<td>5.5 W·m⁻¹K⁻¹</td>
</tr>
<tr>
<td>Mass density</td>
<td>3.17 g·cm⁻³</td>
</tr>
<tr>
<td>Sound velocity</td>
<td>1.1·10⁴ m·s⁻¹</td>
</tr>
<tr>
<td>Specific heat</td>
<td>0.71 J·g⁻¹K⁻¹</td>
</tr>
</tbody>
</table>

Table 4: Properties of bulk SiNₓ.

B.3 Platinum

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity</td>
<td>71.6 W·m⁻¹K⁻¹</td>
</tr>
<tr>
<td>Mass density</td>
<td>19.77 g·cm⁻³</td>
</tr>
<tr>
<td>Sound velocity</td>
<td>2.8·10³ m·s⁻¹</td>
</tr>
<tr>
<td>Specific heat</td>
<td>0.133 J·g⁻¹K⁻¹</td>
</tr>
<tr>
<td>Temperature coefficient of resistance</td>
<td>3.927·10⁻³ K⁻¹</td>
</tr>
</tbody>
</table>

Table 5: Properties of bulk Pt, from [56].
C  Equations

C.1  Device asymmetry

The device asymmetry can be calculated by equating Eqs. 47 and 49 and solving for $G_{b1}/G_{b2}$. The solution is written in terms of the derivatives that are determined experimentally:

$$A = \frac{dT_h}{dP}, B = \frac{dT_s}{dP}, C = \frac{dT_h'}{dP'}, D = \frac{dT_s'}{dP'}.$$  \hfill (77)

where:

$$P = Q_h + Q_L, P' = Q_h' + Q_L'.$$  \hfill (78)

There are two solutions, one of which is negative and thus not physical. The other one is:

$$\frac{G_{b1}}{G_{b2}} = \frac{-ABD + B^2D + BCD - BD^2 + \sqrt{BD(4A(A - B)C(C - D) + BD(A - B - C + D)^2)}}{2A(A - B)D}. \hfill (79)$$

C.2  Radiation view factor

The view factor between the two membranes is approximately equivalent to that between two identical, parallel rectangles as radiation from one membrane can only hit the other if it comes from the side of the membrane that faces towards it. That side is a rectangle of about 0.45x20 µm. Effects of anything other than the membranes, such as the substrate below them are ignored. An analytical expression for the view factor between two identical, parallel rectangles can be found in literature [57]. Define $a$, $b$ and $c$ as the thickness and width of the membranes and the distance in between them respectively. Then choose $X = a/c$ and $Y = b/c$. The view factor becomes:

$$F_{h-s} = \frac{2}{\pi XY} \left( \ln \left[ \frac{(1 + X^2)(1 + Y^2)}{1 + X^2 + Y^2} \right]^{1/2} + X \sqrt{1 + Y^2} \arctan \frac{X}{\sqrt{1 + Y^2}} ight. + Y \sqrt{1 + X^2} \arctan \frac{Y}{\sqrt{1 + X^2}} \left. - X \arctan X - Y \arctan Y \right). \hfill (80)$$