n-Si–p-Si$_{1-x}$Ge$_x$ nanowire arrays for thermoelectric power generation

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The output power of a discrete assembly of n-Si–p-Si$_{1-x}$Ge$_x$ (0 <= x <= 0.4) thermoelectric generators is measured as a function of load resistance. The influence of Ge content and nanowire structures on the performance of thermoelectric devices is evaluated in measurements around room temperature. The nanowire arrays are etched using a metal induced local oxidation and etching process, based on self-assembled Ag nanoparticles and HF. The use of nanowires and SiGe with dimensions smaller than 30 μm is beneficial for an improvement of, at least, a factor of 10 in the output power. However, better performance improvements can be obtained by optimising the thermal and electrical contact resistances at the interfaces. Optimisation of the electrical contact results in a performance boost by a factor of 25.

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1. Introduction

Thermoelectricity (TE) offers an excellent clean energy generation opportunity due to its lack of moving parts and simple fundamental structure based on pn-junctions. Progress in this field was hindered due to the Wiedemans–Franz law that describes the coupling between the electrical and thermal conductivity [1]. The low conversion efficiency and high costs currently limit its practical application. Much effort is still needed to enhance its efficiency and reduce its cost. However, with the introduction of nanotechnology, thermoelectric power generation is attracting renewed attention in the last few decades. It was shown that the replacement of bulk semiconductor materials by nanowires (NWs) can uncouple the electrical σ, and thermal κ conductivity [2] and thus boost thermoelectric performance. Nanostructures have been proven to greatly enhance the thermoelectric figure-of-merit (ZT) because of increased phonon scattering at the interfaces. It is well known that Si bulk, due to its high thermal conductivity, is a poor material for thermoelectric power generation. However, due to its ubiquitous use, research on Si based materials for TE is thriving. It has been demonstrated that single Si nanowires (NWs) exhibit a 60 times higher ZT than Si bulk [3]. Meanwhile, SiGe alloys can also reduce the thermal conductivity κ via alloy scattering [4] without deteriorating the other performance parameters such as Seebeck coefficient S and electrical conductivity σ. SiGe NWs thus promise to offer even better thermoelectric performance than Si bulk or Si NWs. The use of single NWs is an excellent approach to investigate their physical properties in function of geometrical parameters. However, in order to exploit the improvements of nano-materials in thermoelectric systems, a more straightforward structure is needed. We propose to use arrays of vertically upstanding Si or SiGe nanowires attached to a Si substrate as the legs in a thermo-electric generator (TEG). Some groups have already investigated the thermo-electric performance of arrays of nanowires [5].

In this work, we will show our recent research results on the fabrication and thermoelectric characterisation of SiGe nanowire arrays (NWAs) in a pn-junction TEG configuration. The NWAs are arrays of millions (~10$^7$) of parallel upstanding NWs attached to Si bulk, rather than single NWs as studied before.

The manuscript is organised as follows: in Section 2, material preparation will be explained and in Section 3 the set-up and its influence on the measurements. In Section 4 we give the output power as a function of load resistance for different pn-leg TEG configurations including SiGe NWAs with different Ge concentration. In Section 5 we show the influence of optimising the electrical contact characteristics and conclude in Section 6.

2. Material preparation

Three wafers were prepared with a relaxed Si$_{1-x}$Ge$_x$ layer grown epitaxially on lowly doped p-Si (100) substrates using reduced pressure chemical vapour deposition (RP-CVD) [6]. In the first step, a linearly graded relaxed Si$_{1-x}$Ge$_x$ layer (3–4 μm) was deposited to overcome the lattice mismatch between Si and SiGe, followed by a 2 μm thick constant composition layer. The constant composition layer contains x = 20%, 30% and 40% per wafer. EDX measurements confirm the Ge concentration to be respectively 22%, 30.9% and 44.4%. The SiGe layer is unintentionally p-doped.
The resistivity of the p-Si substrate for the SiGe containing samples was measured by the four-point-probe technique on samples from which the SiGe layer was removed and is found to be \( \rho_{\text{Si}} = 2.7 \ \Omega \ \text{cm} \). The resistivity of the material is chosen to be relatively high in order not to interfere with the nanowire fabrication process. For thermo-electric power generation however, the free carrier concentration in the layers should be higher to increase the electrical conductivity. In Section 5, we shall demonstrate the performance improvement of the output power of Si NWAs obtained by decreasing the wafer’s resistivity.

Metal assisted chemical etching (MACE) is known to offer a simple and cost-effective way to prepare large-area arrays with long vertically upstanding crystalline Si NWs. In this process Ag nanoparticles (NPs) are first deposited on the Si surface in a AgNO\(_3\) (0.06 M):HF (40%):H\(_2\)O solution with a volume ratio of 2:5:13, followed by a Si etch in an HF (40%): oxidising agent mixture that is catalysed by the Ag NPs. For the Si NWs prepared for these experiments we have used HF (40%):H\(_2\)O:H\(_2\)O\(_2\) (0.6 M) with a volume ratio of 2:1:1. This etch is selective along the [100] directions, forming crystalline (depending on the concentration of the oxidising agent) NWs with a diameter between 50 and 200 nm. The length of the NWs is controlled by the etch time and the availability of Ag NPs and oxidising agent. After etching, the residual Ag particles are removed by a solution of concentrated HNO\(_3\) (5 M). Though MACE has proven successful with Si, SiGe is easily attacked by oxidising agents such as H\(_2\)O\(_2\), resulting in the fast removal of the SiGe layer during the etching process. Experimental results show that MACE side etching firstly attacks the defect-rich relaxed Si\(_1-x\)Ge\(_x\) buffer layer, under-etching the NW structure [9]. We have adapted the etching process to avoid the removal of the SiGe layers during chemical etching of SiGe NWs. A single stage AgNO\(_3\) (0.06 M):HF (40%) solution with a volume ratio of 1:1 can be used for the etching of SiGe NWs. We have shown that arrays of Si\(_1-x\)Ge\(_x\) NWs with x up to 40% can be fabricated using this 1-step MACE [10]. SEM and energy-dispersive X-ray spectroscopy (EDX) techniques are used to characterise the SiGe containing NWAs. The EDX results indicate that the SiGe NWAs are properly prepared with limited side etching using the 1-step MACE, even for longer etching times. This is illustrated for the 30% SiGe sample for different lengths of the NWs in Fig. 1. Fig. 2a shows an SEM cross section of the NWA. The etch rate decreases non-linearly with increasing Ge concentration for the same etch conditions, given in Fig. 2b for an etch time of 15 min. and for the same chemical recipe. For short etch time, the etch rate is limited by the Ge concentration. For longer etch times, the etch rate is limited by the supply of chemicals and Ag NPs.

3. Measurement set-up

Due to the sub-mm thickness of the semiconductor samples that form the TEG, a set-up has been built to allow contacts for temperature and voltage measurements. A schematic drawing of the setup is given in Fig. 3. Two small Cu blocks, with an area of 2 cm \( \times \) 2 cm and thickness of 0.5 cm, are used as independent bottom contacts to each sample which have each a cross sectional area of 1.5 cm \( \times \) 1 cm. For the NWA side, the effective transport cross sectional area reduces by approximately 50%. A larger Cu block is used at the hot side to form the electric contact between the two semiconductor samples. This places the two semiconductor sam-

Fig. 1. EDX results for the Si\(_{0.7}\)Ge\(_{0.3}\) sample for an etch time of, from left to right 15 min, 60 min and 4 h. The corresponding lengths are 3.5, 11 and 16 \( \mu \)m.

Fig. 2. (a) SEM cross section of a Si\(_{0.6}\)Ge\(_{0.4}\) NWA. (b) The length of the NWs for an etch time of 15 min as a function of Ge concentration etched with the same chemical recipe.
Fig. 3. Schematic drawing of the set-up to measure the thermo-power of the TE leg. The sample is the black and vertically hatched structure between the Cu blocks.

Fig. 4. (a) Measured temperature difference ΔT meas as a function of heater power P meas for a SiGe NWA sample between two Cu blocks without (×) and with (+) Ag foil at the interfaces. The markers are the measurements, the dashed lines are a guide to the eye only. (b) The current–voltage characteristics for the SiGe NWA, the Si NWA and the Si bulk sample. No Ag foil was used in these measurements.

The mechanical pressure contact in this discrete set-up will cause both a thermal as well as an electrical contact resistance. The thermal contact resistance is a result of both the nano/micro roughness of the semiconductor and the metal, as well as the phonon momentum discontinuity between the different materials.

In order to evaluate the impact of these interface resistances, experiments have been performed. It is well known that to reduce the thermal contact resistance a thin layer of Ag foil can be used. This layer reduces the air gaps between the materials and is an excellent thermal conductor. The results of the measurements with and without foil give an indication of the temperature drop that will occur across the interfaces. The results of the temperature difference as a function of the power measured by heat flux sensor – which is placed between bottom copper block and heat sink – is given in Fig. 4a. At the highest thermal input power, the temperature drop across the interfaces is of the order of 50% of the externally measured temperature difference. The electrical performance is measured via current–voltage measurements at room temperature using an Agilent 4155B semiconductor parameter analyser. These measurements show that the Cu–semiconductor pressure contacts have a non-linear character due to the work function difference between semiconductor and Cu and the nano-air gaps at the junction. The extracted resistances are of the order of kΩ in the forward bias direction. The current–voltage characteristics are given in Fig. 4b. The resistance for the NWA samples is smaller since under pressure, the tops of the NWs collapse and form a better contact. The SiGe sample gives an even lower resistance due to the smaller work function difference between SiGe and Cu.

4. TEG measurements

4.1. Measurement of the Seebeck coefficient

For the measurements of the Seebeck coefficient, S, a set-up similar to that in Fig. 3 is used with an electrical open circuit. In order to improve the accuracy of the extraction, the open circuit voltage ΔV is measured for different values of the temperature difference, ΔT across the structure. S is then derived from the gradient: \( S = \frac{\Delta V}{\Delta T} \) of the samples is thus measured with respect to Cu. \( S_{Si} = 1.84 \mu V/K \), negligible compared to S for semiconductors. Since the measurements are done relative to Cu, the gradient of the ΔV–ΔT graphs (see Fig. 5) is opposite to the sign of S of the semiconductor samples. The offset in ΔV for ΔT = 0 K is due to internal electric fields build-up via charge accumulation at the contacts caused by the very high input impedance voltmeter. It is useful to note...
that this offset voltage together with the stability of the voltage measurement at \(D_T = 0\) K, is a good material control parameter. For NWAs with a highly porous character – as a result of the etching process – \(D_V\) was observed to be high and measurements at \(D_T = 0\) K unstable. This is caused by the high resistance of the NWA when porous in character.

**Table 1**

<table>
<thead>
<tr>
<th>Material</th>
<th>(L_{\text{NWA}}) ((\mu m))</th>
<th>(S) (mV/K)</th>
<th>(S_{\text{eff}}) (mV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Si</td>
<td>15</td>
<td>-0.21</td>
<td>-1.05</td>
</tr>
<tr>
<td>p-Si</td>
<td>16</td>
<td>0.22</td>
<td>1.1</td>
</tr>
<tr>
<td>pn-Si</td>
<td>16/15</td>
<td>0.47</td>
<td>2.35</td>
</tr>
<tr>
<td>(Si_{0.8})Ge(_{0.2})</td>
<td>14</td>
<td>1.12</td>
<td>/</td>
</tr>
<tr>
<td>(Si_{0.7})Ge(_{0.3})</td>
<td>12</td>
<td>1.14</td>
<td>/</td>
</tr>
<tr>
<td>(Si_{0.6})Ge(_{0.4})</td>
<td>18</td>
<td>1.01</td>
<td>/</td>
</tr>
</tbody>
</table>

The choice to measure \(S\) without pressure and Ag foil, is imposed by the need to re-measure the same samples in a pn-junction configuration. Due to the combination of Ag foil and pressure on the NWAs, removal of the sample from the set-up also removes the NWAs from the Si substrate as they remain stuck to the Ag foil. The measurement results of the pn junction can also be found in Fig. 5a and Table 1. We expect that the total \(S_{\text{tot}}\) for the pn junction is the sum of that of the individual n and p junction. We find \(S_{\text{tot}}\) = 2.35 mV/K, while the sum \(S_{\text{tot}} = |S_{\text{eff}}| + |S_{\text{eff}}|\) = 2.15 mV/K, reasonably close to the expected value.

Similar measurements have been carried out for the SiGe NWAs for the different Ge concentrations. In this case, samples were not re-used and therefore both Ag foil and a pressure of 250 N could be applied. The results are given in Fig. 5b and Table 1. S of the SiGe NWA samples have a similar magnitude and are also similar to that of Si NWA. This is not surprising as literature shows that \(S\) does not vary as a function of Ge concentration and moreover, the length of the NWAs is much smaller than the thickness of the remaining bulk.

### 4.2. Measurement of the output power

The measurements of the output power, \(P_{\text{out}}\), were done as a function of load resistance, \(R_L\), using the set-up as drawn in Fig. 3. For the n-leg, Si bulk or NWA, as appropriate, was used in all cases. For the p-leg the p-Si was replaced by the SiGe samples. The cross sectional area of all samples was approximately 1.5 cm \(^2\). The lengths of the NWAs were kept at approxi-

**Fig. 5.** Measurement of the Seebeck coefficient. (a) For the individual Si n (dashed) and p (dotted) NWA and the np junction (dashed–dotted) made with the same material. No Ag foil is used and no pressure is applied. (b) For all three SiGe samples containing a SiGe NWA array. Ag foil is used to minimise the temperature drop across the interface and a pressure of 250 N is applied. \(\times: x = 0.2, \gamma: x = 0.3\) and \(+: x = 0.4\).

**Fig. 6.** Output power, \(P_{\text{out}}\), as a function of load resistance, \(R_L\), for four different pn-junction configurations. Labels: \(+: n-Si–p-Si_{0.6}\)Ge\(_{0.4}\); \(\gamma: n-Si–p-Si_{0.7}\)Ge\(_{0.3}\); \(+: n-Si–p-Si_{0.8}\)Ge\(_{0.2}\). (a) Bulk samples. (b) NWA samples.
internal resistance, $R_{\text{int}}$, NWA length, $l_{\text{NWA}}$. The resistivity of the starting wafer is $\rho = 5.6 \, \Omega \cdot \text{cm}$. Labels: +: Si bulk; ×: Si NWA.

5. Optimisation of the Si TEG

As stated before, in order to improve the output power of the TEG based on thin material films, it is not only important to optimise the thin film itself – by including SiGe alloy and NWAs – the contacts to the external world have a severe impact on the performance.

In order to improve the thermal contact resistance, it was shown that Ag foil and pressure are effective in reducing the temperature drop across the interfaces. However, this approach is not a commercially sustainable one. An integrated structure with good thermal contacts is essential.

To improve the electrical contact resistance, standard microelectronics techniques can be applied.

Our approach to improve the contact resistance is to use spin-on-doping (SOD) on the bulk wafers before the NWAs are etched. Since the etch process is sensitive to the doping type and concentration in the wafers, adjustments to the recipe are essential in order to obtain sufficiently long NWAs of good material quality. The SOD approach before etch ensures that the top of all the NWs in the array will be heavily doped. The SOD process is done by spin coating of a boron/phosphorous solution on p/n type silicon surface followed by a 20 min. preheating on a hot plate at 200$^\circ$C and annealing at 900$^\circ$C in argon atmosphere for 20 min. to diffuse the boron/phosphorous into Si.

The output power of thermoelectric devices without and with Ohmic contact doping is given in Fig. 7a and b respectively. An excellent improvement of a factor of 25 in the output power is observed by reducing the contact resistance. We notice that the contact resistance of the bulk is much more reduced than that of the NWAs.

![Fig. 7. Output power, $P_{\text{out}}$ as a function of load resistance, $R_L$ for Si bulk and Si NWA pn TEGs. The resistivity of the starting wafer is $\rho = 5.6 \, \Omega \cdot \text{cm}$. Labels: +: Si bulk; ×: Si NWA. (a) No Ohmic contact doping. (b) Ohmic contact doping.](image)
The length of the NWs is similar to that in Section 4. A limiting factor in the Ohmic contact improvement of the NWA structure is approximately 1/3rd of that of the bulk. This will always impose a limitation on the Ohmic contact improvement of the NWA structure. This is because the contact area to the NWA is approximately 1/3rd of that of the bulk. This will always impose a limitation on the Ohmic contact improvement of the NWA structure. The length of the NWs is similar to that in Section 4. A pressure of 270 N is applied but no Ag foil is used for these measurements.

The second approach to boost the thermoelectric performance is an increase in carrier concentration. Again MACE on heavily doped material poses challenges and the recipe has to be adapted to allow for sufficiently long, good quality NWAs. In Fig. 8 we show the results for a starting wafer with a resistivity of $\rho = 0.01 \Omega \text{cm}$. Approximately 500 times lower than previously used. Pressure on the contacts of 270 N is applied but no Ag foil, nor Ohmic contact doping was used.

An improvement of a factor of ~20 is obtained. For a higher doping, the open circuit voltage decreases due to a decrease of $S$ with increasing carrier concentration. This is imposed by the classical Wiedemann–Franz relationship. Further improvements are possible by using SOD for Ohmic contact doping. Table 3 summarizes some of the performance parameters.

### Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>$\rho$ bulk ((\Omega \text{ cm}))</th>
<th>Contact doping</th>
<th>$P_{\text{out}}$ (nW)</th>
<th>$R_L$ (k(\Omega))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>5.6</td>
<td></td>
<td>0.01</td>
<td>160</td>
</tr>
<tr>
<td>NWA</td>
<td>5.6</td>
<td></td>
<td>0.04</td>
<td>51</td>
</tr>
<tr>
<td>Bulk</td>
<td>5.6</td>
<td>$\sqrt{\cdot}$</td>
<td>0.58</td>
<td>1</td>
</tr>
<tr>
<td>NWA</td>
<td>5.6</td>
<td>$\sqrt{\cdot}$</td>
<td>1.12</td>
<td>1</td>
</tr>
<tr>
<td>Bulk</td>
<td>0.01</td>
<td></td>
<td>0.32</td>
<td>0.75</td>
</tr>
<tr>
<td>NWA</td>
<td>0.01</td>
<td></td>
<td>0.74</td>
<td>0.82</td>
</tr>
</tbody>
</table>

NWA sample. This is because the contact area to the NWA is approximately 1/3rd of that of the bulk. This will always impose a limitation on the Ohmic contact improvement of the NWA structure. The length of the NWs is similar to that in Section 4. A pressure of 270 N is applied but no Ag foil is used for these measurements.

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### References


