Study of the Thermoelectric Properties of Heavily Doped Poly-Si in High Temperature

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Abstract

Poly-Si is a widely used material for thermoelectric devices due to its CMOS compatibility. However, most of the studies focus on room temperature properties of this material. In this paper the authors present experimental results for a temperature range of -50°C to 300°C in which thermoelectric properties of heavily doped n/p-type poly-Si are measured and investigated, including electric resistivity, thermal conductivity and Seebeck coefficient. The experimental results show that the figure of merit of the heavily doped poly-Si increases continuously, indicating better thermoelectric efficiency of the heavily doped poly-Si with higher temperature.

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Structure words: Thermoelectric, heavily doped polysilicon, high temperature, Seebeck coefficient.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZT</td>
<td>Figure of merit of thermoelectric properties</td>
</tr>
<tr>
<td>α</td>
<td>Seebeck coefficient ($\mu V/K$)</td>
</tr>
<tr>
<td>ρ</td>
<td>Electrical resistivity ($\mu \Omega \cdot m$)</td>
</tr>
<tr>
<td>k</td>
<td>Thermal conductivity ($W/m\cdot K$)</td>
</tr>
<tr>
<td>$V_{out}$</td>
<td>Output voltage of a single thermocouple ($V$)</td>
</tr>
<tr>
<td>$\Delta T$</td>
<td>Temperature difference ($K$)</td>
</tr>
<tr>
<td>$R(T)$</td>
<td>Electrical resistance at temperature $T$ ($\mu \Omega$)</td>
</tr>
<tr>
<td>$R(T_0)$</td>
<td>Electrical resistance at original temperature ($\mu \Omega$)</td>
</tr>
<tr>
<td>$R_S$</td>
<td>Sheet resistance ($\Omega \cdot \square$)</td>
</tr>
<tr>
<td>$I_{xy}$</td>
<td>A positive DC current injected into contact $x$ and taken out of contact $y$ ($A$)</td>
</tr>
<tr>
<td>$V_{xy}$</td>
<td>A DC voltage measured between contacts $x$ and $y$ with no externally applied magnetic field ($V$)</td>
</tr>
</tbody>
</table>

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1. Introduction

In recent years, microelectromechanical systems (MEMS) based on complementary metal-oxide semiconductor (CMOS) compatible process are widely utilized for various applications, owing to the advantages of the CMOS compatible process, including small dimensions, light weight, fast response and integrated circuits (ICs) for further signal processing [1]. One of the representative for CMOS-MEMS devices is the thermoelectric device, e.g. thermopile. A thermopile is a group of in series connected thermoelectric strip pair where the Seebeck coefficient is different for materials forming the pair. Due to the Seebeck effect, thermoelectric voltage is generated linearly corresponding to the temperature difference between the hot-junction and the cold-junction of thermopile structure. Thermoelectric devices as a single device have been widely utilized as non-contact temperature sensors, flow sensors, gas sensors, accelerometers and power generators, while the array of thermoelectric devices have been developed as infrared (IR) imaging devices and microspectrometers.

The efficiency of a thermoelectric material is determined by the dimensionless figure of merit [2]

\[ ZT = \frac{\alpha^2 T}{\rho \kappa} \]  

Where \( \alpha \) is the Seebeck coefficient, defined as the thermoelectric voltage produced per degree temperature difference, \( \rho \) is the electrical resistivity, \( \kappa \) is the thermal conductivity, and \( T \) is the temperature [3,4]. Among the reported thermoelectric materials used in thermopiles, Bi\(_2\)Te\(_3\) and Sb\(_2\)Te\(_3\) are the well-known n-type and p-type materials which generate the highest figure-of-merit, i.e., \( ZT \), within 200 °C. However, these materials are not CMOS compatible. For that reason these two materials cannot be integrated into standard CMOS manufacturing lines. Although some thin film metal materials, e.g. nickel and chromium, are also used in thermopiles, their low Seebeck coefficient limits them from achieving high performance. Recently semiconductor based thermopiles have been presented using Germanium (Ge), Silicon carbide (SiC) and polycrystalline silicon (poly-Si) which can be fabricated using CMOS compatible process. Xie Jin et al. have studied the thermoelectric properties of heavily doped poly-Si at room temperature [5]. In this paper a study on the thermoelectric properties of heavily doped poly-Si up to 300°C is presented. The design of the test structures for electric resistivity, thermal conductivity and Seebeck coefficient are presented in Section 2 and the measurement results are presented in Section 3.

2. Experiment

In this paper heavily doped poly-Si was studied because of its good thermoelectric performance [2]. The implantation conditions of the poly-Si test structures used in the experiment are shown below in Table 1. The thickness of the poly-Si is 700nm.

<table>
<thead>
<tr>
<th></th>
<th>Body implantation</th>
<th>Contact implantation</th>
</tr>
</thead>
<tbody>
<tr>
<td>P type</td>
<td>Energy (keV) Dose(cm(^{-2}))</td>
<td>Energy (keV) Dose(cm(^{-2}))</td>
</tr>
<tr>
<td></td>
<td>50 10(^{15})</td>
<td>20 10(^{16})</td>
</tr>
<tr>
<td>N type</td>
<td>120 10(^{15})</td>
<td>40 10(^{16})</td>
</tr>
</tbody>
</table>

In order to study the electric resistivity of the heavily doped poly-Si, we utilized van-der-Pauw structure as shown in figure 1. Four-point method was utilized to get the average resistivity of the poly-Si. The contacts are numbered from 1 to 4 in a counter-clockwise order, beginning at the top-left contact, as shown in figure 1.

The average resistivity of a sample is given by

\[ \rho = R_s t \]  

where \( R_s \) is the sheet resistance and \( t \) is the thickness of the poly-Si, which is 700nm. To make a measurement, a current is applied to flow along one edge of the sample (for instance, \( I_{12} \)) and the voltage across the opposite edge (in this case, \( V_{34} \)) is measured. From these two values, a resistance (for this example, \( R_{12,34} \)) can be found using Ohm’s law:

\[ R_{12,34} = \frac{V_{34}}{I_{12}} \]  

With the same method, \( R_{23,41} \) can also be measured. Then the sheet resistance \( R_s \) can be defined as followed:

\[ e^{-\pi R_{12,34}/R_s} + e^{-\pi R_{23,41}/R_s} = 1 \]  

Additionally, by varying the ambient temperature the temperature coefficients of resistance (TCRs) of the poly-Si are measured by getting different I/V curves.
The Seebeck coefficient and thermal conductance were determined by a cantilever test structure as shown in figure 2, which performs as a single thermocouple using poly-Si and aluminium (Al) as two thermoelectric materials. The cantilever comprises of three layers: thermal SiO$_2$, doped poly-Si and PECVD SiO$_2$, while the narrow Al line connects the hot-junction and cold-junction for electric signal readout. The geometries of the n-type and p-type cantilever test structure are the same. The thickness of poly-Si in the test structure is 700 nm, while the width is 90 $\mu$m and the length is 300 $\mu$m. The width of the Al line is 1 $\mu$m and the thickness is 700 nm. As the theoretical thermal conductance of SiO$_2$ is much lower than doped poly-Si and the dimensions of Al metal line is smaller than the cantilever over almost two orders, it is expected that the cantilever can reflect the thermal conductance of the poly-Si.
In order to eliminate the influence of the thermal conductance of air, all the experiments were carried out in vacuum chamber at a pressure lower than $1 \times 10^{-4}$ mbar with different ambient temperature as shown in figure 3.

![Fig. 3. Vacuum chamber and temperature stabilizer used for experiment](image)

### 3. Experiment results

Figure 4 shows the measurement results of the p-type test structure. In order to observe the thermocouple’s performance, a bias voltage is applied on the microheater. The hot-junction is connected to ground, resulting in a positive output voltage as the Seebeck coefficient of n-type poly-Si is positive. The input voltage can be converted to input power by equation 5.

$$p_{in} = \frac{V_{in}^2}{R_{heater}}$$

![Fig. 4. p-type thermopile test structure characterization (input power vs. output voltage).](image)

Figure 5 shows the testing results of the n-type single thermocouple. The results are opposite to that of the p-type single thermocouple as the Seebeck coefficient of n-type poly-Si is negative.

In order to get the Seebeck coefficient and thermal conductivity of poly-Si, the temperature coefficients of resistance (TCRs) of the poly-Si need to be obtained. Four-point resistance measurement was used to determine TCR of the heavily
doped poly-Si, which is about -0.22%/K and -0.17%/K for n-type poly-Si and p-type poly-Si, respectively. The temperature difference between the cold junction and the hot junction can be derived by using equation 6.

\[ R(T) = R(T_0) \times (1 + TCR \times (T - T_0)) \]  

(6)

where \( R(T) \) is the resistance at temperature \( T \) while \( R(T_0) \) is the resistance at the original temperature.

According to figure 4 and 5, we can get the voltage drop between the cold junction and hot junction. The relationship between temperature difference and the output voltage of the thermocouple can be described by equation 7.

\[ V_{out} = \Delta T(\alpha_1 - \alpha_2) = \Delta T\alpha_{12} \]  

(7)

where \( \Delta T \) is the temperature difference between the two ends of the thermocouple. The end which has a higher temperature is known as the “hot-junction”, while the other end is known as the “cold-junction”. TCR is the temperature coefficients of resistance. Here \( \alpha_1 \) and \( \alpha_2 \) are the Seebeck coefficients of the two materials, and the difference between \( \alpha_1 \) and \( \alpha_2 \) is defined as \( \alpha_{12} \).

Figure 6 shows the calculated Seebeck coefficient of p-type heavily doped poly-Si. According to this figure, the magnitude of the Seebeck coefficient of the p-type heavily doped poly-Si is increasing with temperature but saturates over 200°C. By comparing the Seebeck coefficient of p-type heavily doped poly-Si at -50°C and 200°C, a significant increase can be observed. The Seebeck coefficient of the p-type heavily doped poly-Si increases over 400% at 250 °C temperature difference.

Fig. 5. n-type thermopile test structure characterization (input power vs. output voltage).

Fig. 6. Seebeck coefficient of p-type poly-Si in different temperature
Figure 7 shows the calculated Seebeck coefficient of the n-type heavily doped poly-Si. Similar to the case of p-type poly-Si, the magnitude of the Seebeck coefficient of n-type heavily doped poly-Si increases largely with temperature. The main difference is that the magnitude of the Seebeck coefficient of the n-type heavily doped poly-Si decrease a little over 200 °C. This phenomenon needs further study. In another aspect, the increasing rate of the magnitude of the Seebeck coefficient of the n-type heavily doped poly-Si is not so significant as p-type. The magnitude of the Seebeck coefficient increase only about 150% for this case.

Using equation 6 it is possible to calculate the temperature difference between cold-junction and hot junction. Additionally the thermal conductance can also be calculated. The calculation results show that the thermal conductivity of the heavily doped poly-Si almost do not change with the temperature. The electric resistivity at room temperature, TCR, Seebeck coefficient at room temperature and the thermal conductivity are shown in table 2. With all these parameters the figure of merit ZT, which is the representative parameter, can be determined by equation 1.

<table>
<thead>
<tr>
<th></th>
<th>Electric resistivity ($\mu\Omega$m)</th>
<th>TCR (%/K)</th>
<th>Seebeck coefficient ($\mu$V/K)</th>
<th>Thermal conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-type</td>
<td>13.7</td>
<td>-0.17</td>
<td>137</td>
<td>33.6</td>
</tr>
<tr>
<td>n-type</td>
<td>8.9</td>
<td>-0.22</td>
<td>-118</td>
<td>31.9</td>
</tr>
</tbody>
</table>

Figure 8 shows the figure of merit ZT, of p-type heavily doped poly-Si at different temperature. This figure shows clearly that the ZT of p-type heavily doped poly-Si increases continuously with temperature but does not saturate after 200°C. Although the Seebeck coefficient of the p-type heavily doped poly-Si becomes saturated, the electric resistivity decreases continuously due to the negative TCR of the p-type heavily doped poly-Si.
Figure 9 shows the figure of merit ZT of the n-type heavily doped poly-Si. The results also show continuous increase of ZT in this case. Although the increasing rate is not as significant compared to p-type heavily doped poly-Si, the figure of merit exceeds 0.12, which is close to the case of p-type heavily doped poly-Si.

4. Conclusion

In this paper we have presented the design of test structures to investigate thermoelectric properties of heavily doped poly-Si. Furthermore, experimental results from -50°C to 300°C have been carried out to thermally characterize heavily doped n-type and p-type poly-Si. The measurement results prove that poly Si based thermoelectric devices are able to provide greater performance at higher temperature. This phenomenon provides the possibility to build CMOS compatible thermoelectric devices for relatively high temperature applications.

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References

- Journal articles: