Importance of grain size for nanostructured poly-Si thermoelectric material

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Abstract. Silicon thermoelectric device is one of the promising energy harvesters due to its compatibility with current semiconductor technology and environment, and various types of nanostructured silicon are studied to improve thermoelectric efficiency. In this work, we investigate thermoelectric performance of poly-Si membranes with PnC nanopatterning. The results show that PnC patterning reduces the thermal conductivity of membranes by 60 %, and grain size control enables more efficient reduction. These effects of nanostructure and grain can be combined, and important for high thermoelectric material efficiency.

1. Introduction

Thermoelectric devices promise a practical solution to energy harvesting technology required for remote devices developed by recent industries such as the Internet of Things (IoT). In recent years, much attention has been given to the development of Si-based thermoelectric materials with the hope of replacing the current standard material which is expensive and toxic. While the thermoelectric performance of bulk silicon is extremely low, nanostructured Si have reported large thermal conductivity reduction making a good thermoelectric material[1–3]. Furthermore, it is found that phononic crystal (PnC) nanopatterning impedes heat conduction and enhance the thermoelectric performance efficiently[4].

In this work, we experimentally characterized thermoelectric figure of merit ZT (= S²σT/κ) of poly-Si membrane nanostructured with PnC heading towards power generating device application. Figure 1 shows the schematic of device which can be fabricated in an SOI wafer by conventional CMOS-MEMS process. The device is composed of several p- and n-dope regions and suspended parts, which create in-plane temperature difference from the environmental temperature difference across the chip. Metal wires are arranged like as pi-module, so that each n- and p-dope regions are connected in series electrically and in parallel thermally. Similar device structure was already studied before[5], but the difference in our structure is that thermoelectric membrane is PnC nanostructured to enhance the temperature difference and output power.
2. Methods
We fabricated PnC nanostructures in a 300-nm-thick poly-Si membrane, and measured thermal and electrical conductivities. First, we deposited SiO$_2$ and poly-Si on Si substrate with LPCVD method. Deposition thickness and temperature is 2.5 µm at 425 °C for SiO$_2$ and 300 nm at 625 °C for poly-Si. Next, we implanted the dopant ions, Phosphorous and Boron for n- and p-dope respectively, in top poly-Si layer, and annealed the wafers to activate the carriers. Annealing time and temperatures are 30 minutes at 900 °C for n-dope and 950 °C for p-dope, and measured Hall carrier concentrations are $9.2 \times 10^{19}$ cm$^{-3}$ and $7.2 \times 10^{19}$ cm$^{-3}$ for n- and p-dope, respectively. Next, we deposited 5 µm × 5 µm Aluminium pads on the poly-Si surface by using the electron beam lithography and electron beam evaporator. Consequently, we made two dimensional PnCs, array of vertical holes, in the poly-Si layer by using electron beam lithography and plasma dry etching with SF$_6$ and O$_2$ as gas etchants. At the same time, two slots were also etched which define the width and length of PnC area. Finally, we removed SiO$_2$ layer under the poly-Si with vapor Hydrofluoric acid for thermal measurement samples, and deposited Gold wires for electrical measurement samples. Figures 2 show the scanning electron microscope (SEM) images of fabricated samples for both thermal and electrical measurement, with different hole radius.

![Figure 1. Schematic of membrane based thermoelectric power generator. Suspended parts induce in-plane temperature difference in thermoelectric elements, and PnCs enhance this difference.](image)

![Figure 2. SEM images of fabricated samples (a) for µTDTR measurement and (b) for four probe measurement and detail of PnC with (c) small holes and (d) large holes. The neck size of PnC, distance between adjacent holes, is defined by hole period (a) and radius (r) as $n = a - 2r$.](image)
We measured thermal conductivity of PnCs by means of micro time-domain thermoreflectance (μTDTR). In μTDTR method, we use two different lasers, pulse and probe, and both are focused on the metal pad between PnCs. While pulse laser heats the metal pad, probe signal gives us the reflectivity change of the metal pad caused by temperature rises and drops. From this signal, we obtain the thermal decay time constant of PnCs, and can estimate their thermal conductivities by comparing experiment with finite element model simulation. Detail of measurement can be found in our previous publications[6,7]. We also fabricated the samples for electrical measurement in same wafer, and measured electrical resistance of PnC by four-probe method, and comparing the experimental results with finite element simulation gives us electrical conductivity of PnC. To evaluate the thermoelectric figure of merit, we also measured Seebeck coefficient of a doped poly-Si membrane; measured values are -107 µV/K for n-dope and 147 µV/K for p-dope at 295 K.

3. Measurement results and discussion
Figure 3(a) shows thermal conductivity of nanostructured membrane depending on the PnC hole radius for both n-dope and p-dope samples. Thermal conductivity of membrane without PnC (52.6 W/(m·K) for n-dope and 21.3 W/(m·K) for p-dope) is already reduced from bulk mono crystalline Si value (130 W/(m·K)) because phonons are much scattered by thin film surface and poly crystalline grain boundary. When the PnC is created, thermal conductivity strongly drops from the value of membrane. As hole radius becomes larger, thermal conductivity decreases and reaches more than 60% reduction from membrane for both n- and p-dope. This big reduction is come from strong phonon back scattering on hole surface, and as neck size (space between adjacent holes) become narrower, the effect become larger because the mean free path (MFP) of phonon is strongly limited by the neck part, where phonons are strongly scattered by the sidewall of the holes.

On the other hand, as we show in Figure 3(b), electrical conductivity of PnC does not decrease much, if hole radius is not too large. Since electron MFP in silicon is much shorter than phonon MFP, the impact of PnC pattern on electrical conductivity is less. As a result, we improve the figure of merit, ZT for both n- and p-dope. The values we obtain, however, are still too small to apply the device, further improvement is required especially for n-dope, and it can be achieved by reducing thermal conductivity.

It is known that thermal conductivity of poly crystalline material depends on the grain size[8], so we checked grain size with transmission electron microscope (TEM) to clarify the difference between...
thermal conductivities of n- and p-dope samples. From Figure 4, we found the large difference in grain size, and average grain sizes are estimated as 200 nm and 80 nm for n- and p-dope respectively. Following this, we supposed grain in n-dope Si grew too much during the anneal process causing high thermal conductivity, so we tried short time annealing for another n-dope wafer to make grain size smaller. As shown in Figure 3(a), short annealed n-dope samples have lower thermal conductivity than long annealed ones, it seems we successfully controlled grain growth by changing anneal condition.

Figure 4. Surface TEM image of (a) n-dope and (b) p-dope poly-Si shows grain size of doped poly-Si strongly depends on the dopant.

4. Conclusion
We investigated thermal and electrical property of nanostructured poly-Si membranes for both n- and p-dope. We achieved to improve thermoelectric figure of merit by using proper PnC nanostructure in which phonons are scattered while electrons keep conductive. Furthermore, we showed controlling grain size is important for poly-Si thermoelectric device to reduce thermal conductivity. Since PnC nanostructure and grain boundary impact on thermal conductivity reduction by different mechanism, it is important to combine them for efficient thermoelectric material.

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