Nanoscale



View Article Online

PAPER



Cite this: Nanoscale, 2015, 7, 532

Characterization of nanometer-thick polycrystalline silicon with phonon-boundary scattering enhanced thermoelectric properties and its application in infrared sensors[†]

Huchuan Zhou,^a Piotr Kropelnicki^b and Chengkuo Lee*^a

Although significantly reducing the thermal conductivity of silicon nanowires has been reported, it remains a challenge to integrate silicon nanowires with structure materials and electrodes in the complementary metal–oxide–semiconductor (CMOS) process. In this paper, we investigated the thermal conductivity of nanometer-thick polycrystalline silicon (poly-Si) theoretically and experimentally. By leveraging the phonon-boundary scattering, the thermal conductivity of 52 nm thick poly-Si was measured as low as around 12 W mK⁻¹ which is only about 10% of the value of bulk single crystalline silicon. The *ZT* of n-doped and p-doped 52 nm thick poly-Si was measured as 0.067 and 0.024, respectively, while most previously reported data had values of about 0.02 and 0.01 for a poly-Si layer with a thickness of 0.5 μ m and above. Thermopile infrared sensors comprising 128 pairs of thermocouples made of either n-doped or p-doped nanometer-thick poly-Si strips in a series connected by an aluminium (Al) metal interconnect layer are fabricated using microelectromechanical system (MEMS) technology. The measured vacuum specific detectivity (*D**) of the n-doped and p-doped thermopile infrared (IR) sensors are 3.00 × 10⁸ and 1.83 × 10⁸ cm Hz^{1/2} W⁻¹ for sensors of 52 nm thick poly-Si, and 5.75 × 10⁷ and 3.95 × 10⁷ cm Hz^{1/2} W⁻¹ for sensors of 300 nm thick poly-Si, respectively. The outstanding thermoelectric properties indicate our approach is promising for diverse applications using ultrathin poly-Si technology.

Received 24th July 2014, Accepted 22nd October 2014 DOI: 10.1039/c4nr04184d

www.rsc.org/nanoscale

Nowadays, thermoelectric microdevices using the Seebeck effect, *i.e.*, self-generated voltage due to the temperature difference created between two ends of thermocouple-like structures, are commercialized and demonstrated in diverse applications including non-contact temperature sensing,¹ infrared (IR) focal plane arrays (FPAs),²⁻⁵ air flow sensors,⁶ gas sensors,7 accelerometers8,9 and AC-DC converters.10 On the other hand, the Peltier effect has been deployed in thermoelectric microdevices for thermoelectric cooler applications.11-17 With the aid of microelectromechanical system (MEMS) technology, various configurations of thermoelectric microdevices have been realized on silicon substrates and polymer-based flexible substrates, for example, suspended thermoelectric membranes were created on micro-cavities¹⁸⁻²⁰ and a vertical thermocouple array was formed on polymer substrates.^{21,22} An array of thermocouples connected in a series, a so-called

thermopile, is normally implemented in order to boost the output voltage.

The most widely used thermoelectric materials are the tellurium (Te) alloy with bismuth (Bi), antimony (Sb), and so on,²³⁻³¹ which have a high figure of merit, $ZT = \alpha 2T/\rho k \approx 1$, where α , ρ , k and T are the Seebeck coefficient, electrical resistivity, thermal conductivity and absolute temperature, respectively. It remains a challenging task to have thermoelectric materials with ZT > 1 within a wide operation temperature range.32 CMOS materials such as silicon (Si) and silicon-germanium (SiGe) have been characterized as promising thermoelectric materials. However, the relatively high thermal conductivity of Si (~150 W m⁻¹ K⁻¹) at room temperature makes the ZT of Si low at room temperature. Recently a few studies reported a significant enhancement in ZT of nanostructured Si to reduce the thermal conductivity by enhancing phonon scattering.³³⁻³⁷ The great enhancement of phononboundary scattering leads to a drastic reduction in thermal conductivity when the characteristic length scales are smaller than the mean free path of the phonon at nanometer scale.33 For bulk silicon, the mean free path of the phonon is around 300 nm at room temperature.³⁴ Si nanowires, for instance, have been reported to possess thermal conductivity as low as

^aElectrical and Computer Engineering, National University of Singapore,

⁴ Engineering Drive 3, 117576, Singapore. E-mail: elelc@nus.edu.sg

^bExcelitas Technologies, 8 Tractor Rd., 627969, Singapore

[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/ c4nr04184d

Nanoscale

0.73 W m⁻¹ K⁻¹, which enhances *ZT* by more than 100 times with respect to the typical bulk value.35 Meanwhile, using Si phononic nanomesh structures, a thermal conductivity close to 1.5 W m⁻¹ K⁻¹ was reported.^{36,37} However, it is a great challenge in the fabrication process, from the mass production aspect, to incorporate Si nanowires or Si nanomesh in a planar thermopile structure, which is the mainstream configuration so far. Besides, the thermoelectric characteristics of Si nanowires highly depend not only on their dimensions but also on the nanoscopic surface morphology.³⁸⁻⁴⁰ Thus, top-down fabrication technology can provide reliable and predictable material properties of single crystal Si and polycrystalline Si (poly-Si). The thermal conductivity of single crystal Si with a thickness of about 100 nm has been studied,^{34,41} showing an over 50% reduction in thermal conductivity to around 50 W m⁻¹ K⁻¹. However, this value is still much larger than the thermal conductivity of bulk poly-Si, which is around 30 W m⁻¹ K^{-1,42,43} because the grain boundary scatters phonons, thus leading to a reduction in thermal conductivity.44 Besides, a portion of n-doped dopants segregate to the grain boundaries in poly-Si, also contributing to greater phonon scattering.45 Advanced CMOS manufacturing technology can allow features of a few tens of nanometers and thin poly-Si layers of a few nanometers fabricated in a 12" wafer. In view of the strong needs of high ZT CMOS thermoelectric materials, we investigated ultrathin poly-Si in order to enhance the ZT based on phonon-boundary scattering. Subsequently, a scalable design of the thermopile was fabricated in a CMOS mass production line based on ultrathin polycrystalline Si with optimized ZT and device configurations.

To investigate how the thickness of the thin poly-Si layer affects the *ZT*, micromachined test-keys were deployed to study the thermal conductivity, Seebeck coefficient and electrical resistivity of the n/p-doped poly-Si layer. The test-key is shown in Fig. 1 and the testing setup is the same as the one reported in the authors' previous work.⁵

The Seebeck coefficient and thermal conductance were determined by a cantilever test structure as shown in Fig. 1(a)-(c), which performs as a single thermocouple using poly-Si and aluminium (Al) as the thermocouple pair materials. The cantilever comprises three layers: thermal SiO_{2} , doped poly-Si and plasma enhanced chemical vapor deposition (PECVD) SiO₂, while the narrow Al line connects the hotjunction and cold-junction for electrical signal readout. The geometries of the n-type and p-type cantilever test structures are the same. The thicknesses of the poly-Si in the test structure are 52 nm, 73 nm, 102 nm 123 nm and 300 nm, while the width is 90 µm and the length is 300 µm. The width and the thickness of the Al line are 1 µm and 100 nm, respectively. A micro-heater is arranged at the suspended end to heat up the hot-junction of the test structure while the other end connects to the Si substrate which is kept at ambient temperature, (T_0) as a cold junction. A thermometer made from poly-Si is arranged at the end of the hot-junction to monitor the temperature, T_1 , by monitoring the resistance of the thermometer.



Fig. 1 SEM image (a), optical microscopy image (b), and schematic drawing (c) of the test-key of thermal conductivity; and an optical image of the test-key of electrical resistivity (d).

The thermal conductance, K_c , and Seebeck coefficient, α_{Si} , can be calculated from eqn (1) and (2):

$$K_{\rm c} = \frac{V_{\rm in}^2}{R_{\rm heater}} (T_1 - T_0)^{-1}, \qquad (1)$$

$$\alpha_{\rm Si} = \frac{V_{\rm out}}{T_1 - T_0} + \alpha_{\rm Al},\tag{2}$$

where V_{in} is the voltage applied on the micro-heater, R_{heater} is the electrical resistance of the heater; V_{out} is the output voltage and α_{Al} is the Seebeck coefficient of Al. The magnitude of the Seebeck coefficient of Al is less than 2 so the Al wire will not affect the measured Seebeck coefficient of the poly-Si significantly. The thermal conductivity, on the other hand, will be affected by the Al wire and the SiO₂ layer since the contribution to the overall thermal conductance of the cantilever from Al and SiO₂ is not negligible. Because the thickness and width of Al and SiO₂ are the same for all test-keys and the only difference is the thickness of the poly-Si, it is possible to eliminate the influence of Al and SiO₂.

A van-der-Pauw structure as shown in Fig. 1(d) was used to study the electrical resistivity of the heavily doped poly-Si. The average electrical resistivity of a sample is given by:

$$\rho = R_{\rm s} \times t, \tag{3}$$

where R_s is the sheet resistance and t is the thickness of the poly-Si. To conduct the measurement, we apply a current to flow along one edge of the sample, for instance, I_{12} , where the pad number mark is indicated in Fig. 1(d), and measure the

$$R_{12,34} = V_{34}/I_{12} \tag{4}$$

With the same method, $R_{23,41}$ can also be measured. Then the sheet resistance R_s can be defined as follows:⁵²

$$e^{-\pi R_{12,34}/R_s} + e^{-\pi R_{23,41}/R_s} = 1$$
(5)

Then, the temperature coefficients of resistance (TCRs) of the poly-Si are measured by varying the temperature with a temperature stabilizer and further study of the *I*/*V* curve. TCR describes the temperature dependence of resistance as R(T) = $R(T_0) \times (1 + TCR \times (T - T_0))$, where R(T) is the resistance at temperature *T* while $R(T_0)$ is the resistance at the original temperature T_0 . The measured TCR is -0.20% K⁻¹ and -0.15%K⁻¹ for the n-doped poly-Si and the p-doped poly-Si, respectively. The measured thermal conductivities of the n/p-doped poly-Si with different thicknesses at room temperature are shown in Fig. 2(a). The results show that the thermal conductivity decreases when the poly-Si thickness reduces.

This phenomenon becomes more significant when the thickness is less than 150 nm. By using a frequency-dependent relaxation time to demonstrate the effects of phonon scattering events, Callaway reported a theoretical model with one approximate solution to the Boltzmann transport equation for



Fig. 2 The measured and simulated thermal conductivities of the ultrathin poly-Si (a); and the thermal resistivity of the poly-Si influenced by different kinds of phonon scattering (b) *versus* poly-Si thickness.

phonons in 1959.⁴⁶ Later in 1963, Holland improved this method by taking phonon polarization into account.⁴⁷ Furthermore, A. D. McConnell and her colleagues expanded this model by adding in the study on the effect of grain boundaries and the dopant impurities.⁴⁸

Both mobile carriers and phonons contribute to the overall thermal conductivity of poly-Si as shown in eqn (6):

$$k = k_{\rm e} + k_{\rm p},\tag{6}$$

where k_e is the thermal conductivity induced by electrons and k_p is the thermal conductivity induced by phonons. According to the Wiedemann–Franz law, k_e at a certain temperature, *T*, can be defined by eqn (7) below:

$$k_{\rm e} = \frac{\pi^2 K_{\rm B}^2 T}{3q^2 \rho},\tag{7}$$

where $K_{\rm B}$ is the Boltzmann constant, q is the electron charge and ρ is the electric resistivity of the poly-Si. Since the electric resistivity of the doped poly-Si is in the magnitude of $10^{-5} \Omega$ m,⁴⁴ the estimated value of $k_{\rm e}$ is less than 1 W m⁻¹ K⁻¹ which is not significant compared to the overall thermal conductivity. Therefore, it is reasonable to claim that the phonon scattering events dominate.

Using Callaway and Holland's model, thermal conductivity induced by phonons, k_p , can be calculated with eqn (8) below:

$$k_{\rm p} = \frac{1}{3} \left(\frac{k_{\rm B} T}{h/2\pi} \right)^3 \frac{k_{\rm B}}{2\pi^2} \sum_{j=\rm L, \rm TO, \rm TU} \frac{1}{\nu_j} \int_0^{\theta_j/T} \frac{x_{\omega}^4 e^{x_{\omega}} \tau_j}{\left(e^{x_{\omega}} - 1\right)^2} dx_{\omega}$$
(8)

where x_{ω} is the dimensionless phonon angular frequency which is defined as $x_{\omega} = h\omega/2\pi K_{\rm B}T$, *h* is Planck's constant, $k_{\rm B}$ is the Boltzmann constant, *T* is the temperature and τ_j is the phonon relaxation time. This method presents the phonon scattering events in the longitudinal model and the transverse model, while the transverse model is divided into a low-frequency model and a high-frequency model. The symbols L, TO and TU in eqn (8) refer to the longitudinal model, low-frequency transverse model and high-frequency transverse model, respectively. v_j is the phonon group velocity in different modes. In silicon, $v_{\rm L} = 8.84 \times 10^3$ m s⁻¹, $v_{\rm TO} = 5.86 \times 10^3$ m s⁻¹ and $v_{\rm U} = 2.0 \times 10^3$ m s⁻¹.

The relaxation time τ_j for each model contains several phonon scattering events as shown in eqn (9):

$$\tau_j^{-1} = \sum_i \tau_{j,i}^{-1}.$$
 (9)

Generally, there are phonon-phonon scattering, phononelectron scattering, phonon-boundary scattering and massdifference impurity scattering.⁴³ In comparison to the other three factors, phonon-electron scattering is negligible.⁴⁵ Furthermore, phonon scattering on the grain boundary and segregated dopants also contributes to the relaxation time in the case of the doped poly-Si. Since the thickness we chose is much less than the mean free path of the phonon (~300 nm at room temperature), the phonon-boundary scattering should be the key in this study. The detailed description of the other

Paper

phonon scattering events has been discussed by Holland.⁴⁷ We emphasize the influence of phonon-boundary scattering. First of all, the phonon relaxation time induced by phonon-boundary scattering is shown in eqn (10):

$$\tau_{\text{boundary}}^{-1} = \frac{\nu_{\text{s}}}{d} \left(\frac{1-p}{1+p} \right) \tag{10}$$

where *d* is the thickness of the poly-Si, v_s is an averaged phonon group velocity which can be defined as $v_s^{-1} = (2/v_{TO} + 1/v_L)/3$. And *p* is a parameter with a value between 1 and 0, representing the surface roughness parameter which is the probability of specular reflection from the sample boundary. *p* = 1 means a perfectly smooth surface reflecting all incoming phonons while *p* = 0, on the other hand, represents an entirely rough surface that diffusely scatters all incident phonons like a blackbody.

With the above-mentioned equations, we conducted the simulation to derive the thermal conductivity of the poly-Si using Matlab 2010b. The simulation results of thermal conductivity of both n/p-doped poly-Si with different thicknesses are also shown Fig. 2(a). The thermal conductivity of both n/p-doped poly-Si decreases as the thickness of the poly-Si layer reduces. It matches with the measured data well. From eqn (5), the phonon relaxation time induced by the phonon-boundary scattering event is inversely proportional to the thickness of the poly-Si.

In order to understand how the phonon-boundary scattering affects the overall thermal conductivity, a simulation of the contribution of phonon-boundary scattering to the overall thermal conductivity compared to other phonon scattering events was conducted. Fig. 2(b) shows the contribution of phonon-boundary scattering to the overall thermal conductivity compared to other phonon scattering events. It is clearly observed that the thermal resistivity is dominated by the phonon-boundary scattering when the thickness of the poly-Si layer is less than 100 nm, while the other phonon scattering events are not affected by the change of the poly-Si layer thickness.

Moreover, the electrical resistivity and Seebeck coefficient of the poly-Si layers with different thicknesses were also measured and are shown in Fig. 3(a) and (b). This suggests that these two parameters are intrinsic properties which are subject to doping concentration and do not change with the poly-Si thickness. According to the calculated figure of merit, ZT, (Fig. 3(c)), the n-doped poly-Si has a much higher ZT compared to the p-doped poly-Si among measured data of all 5 kinds of thickness variation in this experiment. This is because the n-doped poly-Si has a relatively lower electrical resistivity and higher Seebeck coefficient compared to the p-doped poly-Si. Besides, the trend of the change of ZT along with the poly-Si thickness variation reflects the trend of the thermal conductivity change regarding poly-Si thickness shown in Fig. 3(a). It is observed that the maxima ZT of 0.067 and 0.024 are obtained for the 52 nm thick n/p-doped poly-Si layer, respectively. Such results show a 116% and 92% incre-



Fig. 3 The electrical resistivity (a), Seebeck coefficient (b) and figure of merit, *ZT*, (c) measured at room temperature.

ment in *ZT* when the thickness of the poly-Si layer decreases from 300 nm to 52 nm. Generally speaking, the *ZT* of bulk poly-Si is around 0.01 because of the relatively high thermal conductivity (\sim 30 W m⁻¹ K⁻¹).^{20,50}

A comparison of the thermoelectric properties measured in this work to other state of the art is shown in Table 1. From the above discussion of the ultrathin poly-Si thermoelectric data, a thermopile using the ultrathin poly-Si layer was developed and characterized. Fig. 4 shows the schematic drawing of the thermopile which possesses a cross-like suspended membrane structure with a coated IR absorber at the center square area. When the thermopile is exposed to IR radiation, the central absorber area absorbs the radiation and turns the radiation power into heat. The heat causes a temperature rise at the central part of the thermopile, *i.e.*, it is defined as the hotjunction of the thermocouple. The other end of the thermocouple in the thermopile, which is connected to the single crystalline Si substrate, is maintained at room temperature during the measurement because of the high thermal conductance and large thermal mass of the Si substrate. As a result,

Table 1 A comparison of the thermoelectric properties measured in this work to other state of the art

Poly-Si type	Thermal conductivity (W mK ⁻¹)	Seebeck coefficient (µV K ⁻¹)	Electrical resistivity (μΩ m)	Figure of merit <i>ZT</i>	Details
n-Type	12.1	-242.1	18.3	0.067	This work: $t = 52$ nm, heavily doped
• •	31.5	-57	8.1	0.004	Bulk, $t > 1 \ \mu m$, intrinsic ⁵⁰
	29.7	-110	8.9	0.014	Bulk, $t \sim 700$ nm, heavily doped ²⁰
p-Type	12.0	182.3	28.9	0.024	This work: $t = 52$ nm, heavily doped
	31.2	103	22.1	0.005	Bulk, $t > 1 \ \mu m$, intrinsic ⁵⁰
	28.4	130	13.7	0.012	Bulk, $t \sim 700$ nm, heavily doped ²⁰



Fig. 4 Schematic drawing of the IR sensor and single thermocouple (not to scale).

there is a temperature difference between the hot-junction and the cold-junction which brings a self-generated voltage between the two ends of the thermopile, *i.e.*, the hot-junction and the cold-junction.

The thermopile comprises 128 pairs of connected thermocouples and the schematic drawing of a single thermocouple is shown in Fig. 4. The doped poly-Si strips are built at the bottom as one material of the thermocouple while Al is another material which also forms an electrical connection between each thermocouple. According to the Seebeck effect, the temperature difference between the two ends of the thermocouple will induce a voltage drop which can be read out through the contact pads.

The thermopile structure is fabricated using the CMOS process. Fig. 5 illustrates the fabrication process of the ultrathin poly-Si based thermopile IR sensor. The process started with an 8-inch bare Si wafer with 40 nm of thermal SiO₂ on top (Fig. 5(a)). Then, the poly-Si of different thicknesses was deposited at 760 °C and doped as n-type and p-type with different wafers. The thickness variation of the poly-Si was the same as the test-key presented earlier. After that, the poly-Si were patterned with photo-lithography and plasma etching (Fig. 5(b)). Subsequently, a 30 nm thick SiO_2 was built as an electrical isolation layer by plasma enhanced chemical vapor deposition (PECVD); then the contact was open on SiO_2 and an additional surface heavy implantation was conducted to reduce the electrical contact resistivity between the poly-Si and Al; after the contact implantation the whole wafer was annealed under N₂ at 1050 °C for 30 minutes (Fig. 5(c)). After annealing, Al was deposited and patterned followed by further annealing under N2 at 420 °C for 30 minutes to achieve a



Fig. 5 Process flow of the device. The process starts with Si substrate covered by LPCVD SiO₂ (a); then poly-Si strip is deposited, doped and patterned (b); then SiO₂ electric isolation layer was deposited, and contact *via* was opened (c); then Al wire was deposited and patterned (d); then SiO₂ passivation layer was doped, and the contact pad was open followed by XeF₂ release (e); CNT/SU-8 IR absorber was deposited in the end (f).

better electrical connection (Fig. 5(d)). After that we deposited another 30 nm PECVD SiO_2 passivation layer and then opening of the contact area of the Al pad; after that release slots and holes were opened and the whole structure was released using XeF₂ (Fig. 5(e)). After releasing the structure, a drop of solution comprising carbon nanotubes (CNTs) mixed with SU-8 was deposited at the central part of the thermopile as a broadband IR absorber (Fig. 5(f)).

The fabricated device is shown in Fig. 6. The parts which seem unsmooth in Fig. 6(a) are due to the stress induced by the SiO₂ and poly-Si layers. This stress can be reduced by using Al₂O₃ as the dielectric layer instead of SiO₂. However, Al₂O₃ possesses much higher thermal conductivity compared to SiO₂, which would hinder the performance of the thermopile. Even though the stress, induced by SiO₂ in Fig. 6(a), seems large, the SiO₂ membrane can provide enough mechanical strength to this structure.⁴⁹ This is the reason the authors chose SiO₂ as the dielectric layer to build the thermopile. The scanning electron microscopy (SEM) image and the Fourier transform infrared spectroscopy (FTIR) characterization of the CNT/SU-8 mixture absorber are shown in Fig. 7(a). As shown in this figure, the surface of the CNT/SU-8 mixture absorber is not smooth. This is due to the manual process of coating the absorber



Fig. 6 Optical microscopy image of the thermopile structure without the absorber coating (a); SEM image of the zoomed-in view (b).

onto the IR thermopile. The absorption of IR radiation is very high, up to 98.5% from 2 μm to 8 $\mu m.$

In order to characterize the performance of the thermopile IR sensor using ultrathin poly-Si, an electrical measurement is conducted using a micro-heater placed at the central part of the thermopile to mimic the IR radiation as shown in Fig. 6(b). According to our previous work,⁴⁹ the use of a micro-heater to simulate the IR radiation only introduces 1% difference.

The efficiency of a thermopile is usually evaluated by two parameters: the responsivity, R_v , and the specific detectivity, D^* . R_v presents the efficiency of converting heat to electricity, while D^* stands for how precise the sensor can detect.²⁰ The definitions of R_v and D^* are shown as follows:

$$D^* = R_{\rm v} \sqrt{A\Delta f} / V_{\rm n}, \tag{12}$$

where V_{out} is the output voltage and P_{in} is the infrared power applied to the thermopile; *A* is the IR absorption of the integrated absorber; Δf is the frequency bandwidth of the read out system, and V_{n} is the noise equivalent voltage.

The electrical testing was conducted at room temperature and the testing results of the n-doped and p-doped poly-Si based thermopile are shown in Fig. 8. The results of the experiment conducted in a vacuum are shown in Fig. 8(a), the thermopile with the thinnest (52 nm) poly-Si layer, no matter whether n-doped or p-doped, possesses the highest R_v . The R_v of the thermopile with 52 nm thick n-doped poly-Si is 1000.1 VW⁻¹ while the R_v of the thermopile with 300 nm thick n-doped poly-Si is 105.8 VW⁻¹, which indicates an 845% improvement by reducing the poly-Si thickness. Similarly, the thermopile using p-doped poly-Si also shows a great improvement with respect to thinner poly-Si. R_v is 772.5VW⁻¹ and 84.4VW⁻¹ for the p-doped thermopile with 52 nm thick poly-Si and 300 nm thick poly-Si, where an 815% improvement is observed for the thinner p-doped poly-Si.

In order to study the influence of air on the performance of the thermopile, the authors conducted the measurement again at atmospheric pressure and the results are shown in Fig. 8(b). In contrast to the measurement results in a vacuum,



Fig. 7 SEM image (a) and FTIR measurement results (b) of the CNT/ SU-8 mixture absorber.



Fig. 8 Electrical testing measured responsivity (R_v) of n/p-doped poly-Si in a vacuum (a) and at atmospheric pressure (b).

Paper

the R_v of all thermopiles decreased by over an order of magnitude. Besides, the enhancement of R_v , caused by the reduction of the poly-Si thickness, is not so significant compared to the results achieved in a vacuum. This is because the thermal conductivity of air dominates when the thermopile is working at atmospheric pressure. The R_v results of the n-doped and p-doped poly-Si with a thickness of 52 nm decreased to 24.8 VW⁻¹ and 19.0 VW⁻¹, respectively. Compared to the $R_{\rm v}$ achieved in the vacuum test, the reduction is over 97%. On the other hand, the R_v measurements of the n-doped and p-doped poly-Si with a thickness of 300 nm do not show such great decrease, as the results were 23.6 VW^{-1} and 18.1 VW^{-1} , respectively, with a reduction of only about 78% compared to the case in a vacuum. Since the thermal conductance from air is the same for all thermopiles, due to the same surface area, the reduction in thermal conductance of the structure is not so significant to the overall thermal conductance.

After the characterization of the thermopile structure, the authors conducted an IR radiation test using a blackbody with a temperature of 470 °C as the IR radiation source. According to the Planck's curve, the radiation peak is around 3.9 μ m, which is in the absorption range of the CNT/SU-8 mixture



Fig. 9 IR response of the n-doped poly-Si (a) and the p-doped poly-Si (b) thermopile with different chopper frequencies.

absorber. The details of the testing setup of the radiation test has been reported in our previous work.⁵

The IR radiation test was conducted in a vacuum and only at room temperature. The results are shown in Fig. 9(a) and (b). It is clear that the thermopile IR sensor using 52 nm thick poly-Si has the highest output. For the n-doped and p-doped microdevices the values are approximately 890% and 700% compared to that of the thermopile IR sensor using 300 nm thick poly-Si, respectively. As shown in Fig. 9(a) and (b), the output voltage decreases with a higher chopper frequency because the thermopile needs time to heat up. The thermal time constant of the thermopile IR sensor can be decided by the time required to reach 63% of the maximum detector output voltage.⁵¹ Using the data shown in Fig. 9(a) and (b) the calculated time constant of the thermopile IR sensors with different poly-Si thicknesses and doping types are shown in Table 2.

Since the absorption of the IR absorber is not 100%, the responsivity, R_v , of the IR sensor is different from the R_v measured by electrical testing. Using Planck's equation, the authors estimated that the power applied on the IR sensor is 29.7 μ W. Then, the R_v of the IR sensor was derived with the estimated radiation power and output voltage shown in Fig. 10(a).

According to the data shown in this figure, the R_v of the IR sensor is only slightly smaller than the perfect R_v from the electrical test. The overall emissivity, ε , of the IR sensor is further calculated using eqn (13)

$$\varepsilon = \frac{R_{\rm v_IR}}{R_{\rm v_electrical}},\tag{13}$$

where $R_{v_{-IR}}$ is the R_v of the IR sensor and $R_{v_{-}electrical}$ is the perfect R_v acquired from the electrical test. The average overall emissivity was calculated as 95%.

The overall series of electrical resistances of all the sensors were also measured and the results are shown in Table 3. Since there is no current flow through the microdevice, there is no 1/f noise but only Johnson noise of the thermopile IR. The Johnson noises are estimated from the measured series of electrical resistances and are shown in Table 3. Then the specific detectivity, D^* , of each thermopile IR sensor was further estimated as shown in Fig. 10(b). The thermopile IR sensors with thinner poly-Si possess higher D^* , which is the same as the testing results of R_v . The D^* of the n-doped poly-Si with thicknesses of 52 nm and 300 nm are 3.00×10^8 and 5.75×10^7 cm Hz^{1/2} W⁻¹, respectively, while the D^* of the p-doped poly-Si with thicknesses of 52 nm and 300 nm are 1.83×10^8

Table 2	Calculated time	constants of the	thermopile IR	sensors
---------	-----------------	------------------	---------------	---------

Thickness of poly-Si (nm)		52	73	102	123	300
Time constant in a vacuum (ms) Time constant at atmospheric pressure (ms)	n-Doped p-Doped n-Doped p-Doped	87 87 0.85 0.85	77 78 0.89 0.89	65 66 0.94 0.94	58 60 0.98 0.98	30 32 1.27 1.27



Fig. 10 Measured responsivity (a) and specific detectivity D^* (b) in a vacuum.

 Table 3
 Measured series
 of
 electrical
 resistances
 and
 estimated

 Johnson noise from the thermopile IR sensors
 Image: sensors
 <td

Thickness of poly-Si (nm)		52	73	102	123	300
Series of electrical resistance $(10^6 \Omega)$ Estimated Johnson noise (μ V Hz ^{-1/2})	n-Doped p-Doped n-Doped p-Doped	1.91 2.91 0.18 0.22	1.43 2.14 0.15 0.19	1.09 1.60 0.13 0.16	0.94 1.37 0.12 0.15	0.52 0.70 0.09 0.11

and 3.95×10^7 cm Hz^{1/2} W⁻¹, respectively. As shown above, the enhancement in *D** of the n-doped and p-doped thermopiles with ultrathin poly-Si is 421% and 364%, respectively. However, compared with the stated value of *R*_v, we do not see such significant enhancement in *D**, because of the higher noise induced by the increase of electrical resistance of the thinner poly-Si strip.

The radiation test was also conducted at atmospheric pressure and the results are shown in Fig. 11 and 12. As shown in Fig. 11(a) and (b), the response of the sensor becomes much faster due to the large thermal conductance caused by air. The calculated time constant of the IR sensor is shown in Table 2 as well. The main difference of the IR test results at atmospheric pressure, compared to the data measured in a vacuum, is that D^* increases along with the thickness of poly-Si. As discussed above, since the thermal conductance of air



Fig. 11 IR response of the n-doped poly-Si (a) and the p-doped poly-Si (b) thermopile with different chopper frequencies.



Fig. 12 Measured responsivity (a) and specific detectivity D^* (b) at atmospheric pressure.

dominates in this case, the reduction of the overall thermal conductivity caused by the decreasing poly-Si thickness is not as significant as in a vacuum. Therefore, the enhancement of R_v is also not so significant. The noise, on the other hand, increases with the reducing thickness of poly-Si. That is the reason why the D^* , shown in Fig. 12(b), shows a different trend when the sensor is working at atmospheric pressure.

By improving the straightforward fabrication approach, the thermoelectric properties of ultrathin poly-Si have been obtained because of the phonon-boundary scattering effect. This fabrication process is fully CMOS compatible without using other advanced nanofabrication technologies, *e.g.*, electron beam lithography (EBL), *etc.* The demonstrated R_v and D^* results of the thermopile IR sensor are promising for various applications.

Conclusion

In this paper, the authors studied the thermoelectric properties of ultrathin poly-Si, showing an impressive enhancement in ZT by decreasing the thickness of the poly-Si to reduce the thermal conductivity, due to strong phonon-boundary scattering. The maxima ZT of 0.067 and 0.024 were obtained for the 52 nm thick n- and p-doped poly-Si layers, respectively. Such results show a 116% and 92% increment in ZT when the thickness of the poly-Si layer decreases from 300 nm to 52 nm. Then, the design, fabrication and testing of the thermopile IR sensor, using ultrathin poly-Si, was presented to demonstrate its application in thermoelectric devices. The measured R_v of the IR sensors using 52 nm n- and p-doped poly-Si were 1000.1 VW^{-1} and 772.5 VW^{-1} in a vacuum, respectively. D^* of the IR sensors using 52 nm n- and p-doped poly-Si were 3.00×10^8 and $1.83\times 10^8~\text{cm}~\text{Hz}^{1/2}~\text{W}^{-1}\text{,}$ respectively. These results illustrate that the R_v of the thermopile IR sensor using 52 nm poly-Si is improved over 845% and 815% compared to the sensor using 300 nm poly-Si for n-doped and p-doped in a vacuum, respectively. While the D^* of the thermopile IR sensor using 52 nm poly-Si was improved by 421% and 364% in a vacuum compared to the sensor using 300 nm poly-Si for n-doped and p-doped. This result indicates the advantage of the poly-Si with a thickness in the nanometer scale as a promising thermoelectric material.

Acknowledgements

The authors acknowledge the financial support from research grants of, SinBerBEST (WBS: R-263-000-A34-592) "TinyCO2 project: Enabling CO2 Sensing at the Millimeter Scale and Ultra-Low Cost for Distributed HVAC Sensing/Control" and AcRF Tier 2 -MOE2012-T2-2-154 (WBS: R-263-000-A59-112) at the National University of Singapore, and the National Research Foundation (NRF) CRP project 'Self-Powered Body Sensor Network for Disease Management and Prevention Oriented Healthcare' (R-263-000-A27-281).

Notes and references

- 1 S. Suman, M. Gaitan, Y. Joshi and G. G. Harman, *IEEE Trans. Adv. Packag.*, 2005, **28**(4), 685–693.
- 2 C. H. Du and C. Lee, Jpn. J. Appl. Phys., 2002, 41(6S), 4340.
- 3 C. H. Du and C. Lee, *Jpn. J. Appl. Phys.*, 2000, **39**(12S), 168–178.
- 4 C. H. Du and C. Lee, in *Design, Characterization, and Packaging for MEMS and Microelectronics, Proc. SPIE*, ed. B. Courtois and S. N. Demidenko, Gold Coast, Australia, October 1999, vol. 3893, pp. 116–126.
- 5 H. Zhou, P. Kropelnicki and C. Lee, J. Microelectromech., 2014, DOI: 10.1109/JMEMS.2014.2322675.
- 6 N. T. Nguyen, Flow Meas. Instrum., 1997, 8(1), 7-16.
- 7 C. Hagleitner, A. Hierlemann, D. Lange, A. Kummer, N. Kerness, O. Brand and H. Baltes, *Nature*, 2001, 414(6861), 293–296.
- 8 U. A. Dauderstädt, P. H. S. De Vries, R. Hiratsuka and P. M. Sarro, *Sens. Actuators, A*, 1995, **46**(1), 201–204.
- 9 V. Milanović, E. Bowen, M. E. Zaghloul, N. H. Tea, J. S. Suehle, B. Payne and M. Gaitan, *Appl. Phys. Lett.*, 2000, 76(4), 508–510.
- 10 M. Klonz, IEEE Trans. Instrum. Meas., 1987, 1001(2), 320-329.
- 11 F. J. DiSalvo, Science, 1999, 285(5428), 703-706.
- 12 J. F. Li, W. S. Liu, L. D. Zhao and M. Zhou, NPG Asia Mater., 2010, 2(4), 152–158.
- 13 M. S. Dresselhaus, G. Chen, M. Y. Tang, R. Yang, H. Lee, D. Z. Wang, Z. F. Ren, J. P. Fleurial and P. Gogna, *Adv. Mater.*, 2007, **19**(8), 1043–1053.
- 14 T. C. Harman, P. J. Taylor, M. P. Walsh and B. E. LaForge, *Science*, 2002, 297(5590), 2229–2232.
- 15 G. J. Snyder and E. S. Toberer, *Nat. Mater.*, 2008, 7(2), 105– 114.
- 16 T. M. Tritt and M. A. Subramanian, *Mater. Res. Soc. Symp.* Proc., 2006, 31(03), 188–198.
- 17 L. E. Bell, Science, 2008, 321(5895), 1457-1461.
- 18 J. Xie, C. Lee, M. F. Wang and J. M. Tsai, *Microsyst. Technol.*, 2011, 17(1), 77–83.
- 19 J. Xie, C. Lee and H. Feng, J. Microelectromech. Syst., 2010, 19(2), 317–324.
- 20 J. Xie, C. Lee, M. F. Wang, Y. Liu and H. Feng, J. Micromech. Microeng., 2009, 19(12), 125029.
- 21 W. Glatz, S. Muntwyler and C. Hierold, *Sens. Actuators, A*, 2006, **132**(1), 337–345.
- 22 H. Yousef, K. Hjort and M. Lindeberg, J. Microelectromech. Syst., 2007, **16**(6), 1341–1348.
- 23 Y. Lan, A. J. Minnich, G. Chen and Z. Ren, Adv. Funct. Mater., 2010, 20(3), 357–376.
- 24 Y. Pei, J. Lensch-Falk, E. S. Toberer, D. L. Medlin and G. J. Snyder, *Adv. Funct. Mater.*, 2011, 21(2), 241–249.
- 25 S. N. Girard, K. Schmidt-Rohr, T. C. Chasapis,
 E. Hatzikraniotis, B. Njegic, E. M. Levin, A. Rawal,
 K. M. Paraskevopoulos and M. G. Kanatzidis, *Adv. Funct. Mater.*, 2013, 23(6), 747–757.

- 26 L. Hu, T. Zhu, X. Liu and X. Zhao, *Adv. Funct. Mater.*, 2014, 24(33), 5211–5218.
- 27 N. Peranio, E. Leister, W. Töllner, O. Eibl and K. Nielsch, *Adv. Funct. Mater.*, 2012, 22(1), 151–156.
- 28 S. Kastbjerg, N. Bindzus, M. Søndergaard, S. Johnsen, N. Lock, M. Christensen, M. Takata, M. A. Spackman and B. B. Iversen, *Adv. Funct. Mater.*, 2013, 23(44), 5477–5483.
- 29 E. S. Toberer, A. Zevalkink, N. Crisosto and G. J. Snyder, *Adv. Funct. Mater.*, 2010, **20**(24), 4375–4380.
- 30 B. A. Cook, M. J. Kramer, J. L. Harringa, M. K. Han, D. Y. Chung and M. G. Kanatzidis, *Adv. Funct. Mater.*, 2009, 19(8), 1254–1259.
- 31 S. K. Bux, R. G. Blair, P. K. Gogna, H. Lee, G. Chen, M. S. Dresselhaus, R. B. Kaner and J. P. Fleurial, *Adv. Funct. Mater.*, 2009, **19**(15), 2445–2452.
- 32 D. L. Medlin and G. J. Snyder, Curr. Opin. Colloid Interface Sci., 2009, 14(4), 226–235.
- 33 C. Dames and G. Chen, in *ThermoelectricsHandbook: Macro* to Nano, ed. D. M. Rowe, CRC Press, Cleveland, 2006, ch. 42.
- 34 Y. S. Ju and K. E. Goodson, Appl. Phys. Lett., 1999, 74(20), 3005–3007.
- 35 A. I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J. K. Yu,
 W. A. Goddard III and J. R. Heath, *Nature*, 2008, 451(7175),
 168–171.
- 36 J. K. Yu, S. Mitrovic, D. Tham, J. Varghese and J. R. Heath, *Nat. Nanotechnol.*, 2010, 5(10), 718–721.
- 37 J. Tang, H. T. Wang, D. H. Lee, M. Fardy, Z. Huo, T. P. Russell and P. Yang, *Nano Lett.*, 2010, **10**(10), 4279– 4283.

- 38 A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar and P. Yang, *Nature*, 2008, 451(7175), 163–167.
- 39 D. Li, Y. Wu, P. Kim, L. Shi, P. Yang and A. Majumdar, *Appl. Phys. Lett.*, 2003, 83(14), 2934–2936.
- 40 R. Chen, A. I. Hochbaum, P. Murphy, J. Moore, P. Yang and A. Majumdar, *Phys. Rev. Lett.*, 2008, **101**(10), 105501.
- 41 W. Liu and M. Asheghi, J. Heat Transfer, 2006, 128(1), 75-83.
- 42 F. Volklein and H. Balles, J. Microelectromech. Syst., 1992, 1(4), 193–196.
- 43 O. M. Paul, J. Korvink and B. Henry, *Sens. Actuators, A*, 1994, **41**(1), 161–164.
- 44 S. Uma, A. D. McConnell, M. Asheghi, K. Kurabayashi and K. E. Goodson, *Int. J. Thermophys.*, 2001, 22(2), 605– 616.
- 45 M. M. Mandurah, K. C. Saraswat, C. R. Helms and T. I. Kamins, *J. Appl. Phys.*, 1980, **51**(11), 5755–5763.
- 46 J. Callaway, Phys. Rev., 1959, 113(4), 1046.
- 47 M. G. Holland, Phys. Rev., 1963, 132(6), 2461.
- 48 A. D. McConnell, S. Uma and K. E. Goodson, J. Microelectromech. Syst., 2001, 10(3), 360–369.
- 49 H. Zhou, P. Kropelnicki, J. M. Tsai and C. Lee, *J. Micromech. Microeng.*, 2013, 23(6), 065026.
- 50 M. Strasser, R. Aigner, C. Lauterbach, T. F. Sturm, M. Franosch and G. Wachutka, *Sens. Actuators, A*, 2004, 114(2), 362–370.
- 51 D. Xu, B. Xiong and Y. Wang, J. Microelectromech. Syst., 2010, 19(6), 1331-1340.
- 52 L. J. van der Pauw, Philips Res. Rep., 1958, 13, 1-9.