Novel thermoelectric materials based on boron-doped silicon microchannel plates

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ABSTRACT

The thermoelectric properties of boron-doped silicon microchannel plates (MCPs) were investigated. The samples were prepared by photo-assisted electrochemical etching (PAECE). The Seebeck coefficient and electrical resistivity at room temperature (25 °C) were measured to determine the thermoelectric properties of the samples. In order to decrease the very high resistivity, boron doping was introduced and by modulating the doping time, a series of samples with different resistivity as well as Seebeck coefficient were obtained. Boron doping changed the electrical resistivity of the samples from $1.5 \times 10^3 \Omega \cdot cm$ to $5.8 \times 10^{-3} \Omega \cdot cm$, and the absolute Seebeck coefficient deteriorated relatively slightly from $674 \mu V/K$ to $159 \mu V/K$. According to the Seebeck coefficient and electrical conductivity, the power factor was calculated and a peak value of $4.7 \times 10^{-3} \text{mW m}^{-1} \text{K}^{-2}$ was obtained. The results indicate that silicon MCPs doped with boron are promising silicon-based thermoelectric materials.

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1. Introduction

Thermoelectric materials are able to convert heat to electricity and commonly used in cooling and refrigeration applications [1]. The research on thermoelectric materials is growing steadily because of recently demonstrated advances and strong global demand for cost-effective, pollution-free energy conversion [2–5]. The most widely used thermoelectric material, bismuth telluride, has the best thermoelectric properties at around room temperature. However, the application of bismuth telluride and its alloys to energy generation is hampered by limited availability, low stability, and high manufacturing cost. Bulk silicon, which benefits from the well-developed microfabrication technology, is not a proper thermoelectric material on account of its high thermal conductivity of about $150 \text{W m}^{-1} \text{K}^{-1}$ at room temperature [6]. However, recent work has shown that silicon nanowires that possess reduced thermal conductivity and enhanced thermoelectric efficiency due to the quantum confinement effect inherent to nanomaterials may solve the problem [7–9]. Unfortunately, their weak mechanical strength and the difficulty to make good electrical connections are challenges for large scale implementation. On the other hand, porous silicon with randomly distributed pores has a low thermal conductivity of $0.1 \text{W m}^{-1} \text{K}^{-1}$ [10], but the electronic structure of disordered porous silicon yields poor electrical conductivity [11]. To overcome these problems, silicon microchannel plates (MCPs) may be viable because they exhibit good mechanical strength, easily-modulated electrical conductivity, and low thermal conductivity arising from the porous structure. For instance, Sun et al. have recently demonstrated the anisotropic thermoelectric properties of silicon MCPs [12]. In this work, a novel thermoelectric material based on boron-doped silicon MCPs is described and the power factor of the materials with the proper doping is found to be as high as $4.7 \times 10^{-3} \text{mW m}^{-1} \text{K}^{-2}$.

2. Experimental details

The silicon MCPs were prepared by photo-assisted electrochemical etching (PAECE). The starting substrate was a p-type <100> $2–9 \Omega \cdot cm$, single-side-polished silicon wafer with a thickness of 500 μm. The wafer was first thermally oxidized to form a $\text{SiO}_2$ layer of 300 nm and then patterned using lithography to define 3 μm × 3 μm square open regions on the front side. A buffered hydrofluoric acid solution was used to etch the windows in the oxide layer. Pyramidal notches serving as whole nucleation centers for anodizing were subsequently created by tetramethyl ammonium hydroxide etching. The silicon MCPs were then formed by PAECE in a hydrofluoric acid solution diluted with DMF and deionized water. After etching for 8 h, the silicon microchannel plate layer was automatically broken off from the substrate. The microstructure of the samples was examined by scanning electron microscopy (SEM).

The samples were then doped with boron at 1180 °C, and the doping time was varied between 0.5 and 5 h. Nitrogen was used as the protective gas to prevent oxidation and borosilicate glass was adopted as the diffusion source. The electrical resistivity of the doped samples was determined by a four point probe.

The Seebeck coefficient of samples was determined from the thermoelectromotive force ($\Delta V$) and temperature difference ($\Delta T$) by

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\[ S = \frac{\Delta V}{\Delta T} \]. The time evolution of the thermoelectromotive force was monitored by a digital multimeter while the temperature was measured by a thermocouple.

3. Results and discussion

Fig. 1 depicts the surface and cross-sectional views of the silicon MCPs on the microscale. The square pores about 5 \( \mu m \times 5 \mu m \) in size are ordered and distributed evenly with a spacing of about 1 \( \mu m \), as shown in Fig. 1(a). The thickness of the sample is about 150 \( \mu m \) as shown in Fig. 1(b). In addition, the inset in Fig. 1(b) shows the macroscopic image of the silicon MCP and the substrate.

The sample without boron doping has a high electrical resistivity of \( 1.5 \times 10^5 \Omega \text{ cm} \), which is comparable to that of intrinsic silicon \( (2.5 \times 10^5 \Omega \text{ cm at room temperature}) \). Generally speaking, p-type silicon has a positive Seebeck coefficient whereas intrinsic silicon and n-type silicon have negative values. The Seebeck coefficient of the undoped sample is \( -674 \mu V/K \) which is similar to that of intrinsic silicon but not p-type silicon. It can be attributed to the depletion of carriers after the PAECE process. The very high resistivity plagues thermoelectric applications of the silicon MCPs. However, boron doping which is commonly practiced in microelectronics can decrease the resistivity effectively and the doping concentration can be adjusted by varying the time. The relationship between the doping time and resistivity is displayed in Fig. 2. It can be observed that the resistivity diminishes dramatically after boron doping by about 5 to 7 orders of magnitude. In addition, there is a significant reduction in the resistivity when the doping time increases from 0.5 h to 1 h and longer. The inset in Fig. 2 shows a magnified graph of this region in which the resistivity is \( 5.8 \times 10^{-3} \Omega \text{ cm} \) after undergoing boron doping for 5 h.

It is well known that the Seebeck coefficient is sensitive to the electrical resistivity or the conductivity. The absolute values of the measured Seebeck coefficient of the samples with and without boron doping at room temperature are shown in Fig. 3(a) as a function of electrical conductivity. The Seebeck coefficient decreases with increasing conductivity, a trend generally observed from common semiconductor materials [13]. It should be noted that the samples after boron doping have a positive Seebeck coefficient. Furthermore, the undoped sample has the maximum absolute Seebeck coefficient of 674 \( \mu V/K \) and a close to zero conductivity. As the conductivity of the boron-doped samples increases from \( 8.4 \times 10^{-1} \text{ S cm}^{-1} \) to \( 1.72 \times 10^2 \text{ S cm}^{-1} \), the

![Fig. 1. SEM images: (a) surface and (b) cross-section of silicon MCP as well as the macroscopic image of the inset.](image)

![Fig. 2. Relationship between the doping time and electrical resistivity of boron-doped silicon MCP with the inset showing the magnified graph from 1 h to 5 h.](image)

![Fig. 3. Plots of (a) absolute Seebeck coefficient of the samples with and without doping versus the electrical conductivity and (b) the power factor related to the electrical conductivity of the doped samples with the Seebeck coefficient listed.](image)
Seebeck coefficient varies from 240 μV/K to 159 μV/K correspondingly. It suggests that boron doping can enhance the conductivity of the silicon MCPs significantly while the decrease in the absolute value of the Seebeck coefficient is comparatively small. To evaluate the thermoelectric characteristics of the samples with different conductivity values, the power factor \((PF)\) can be calculated by the following relationship:

\[
PF = S^2\sigma, \quad (1)
\]

where \(S\) is the Seebeck coefficient and \(\sigma\) is the electrical conductivity. Fig. 3(b) shows the conductivity dependent power factor of the boron-doped samples. The relationship between the Seebeck coefficient and conductivity is also described. It can be observed that the power factor increases with higher conductivity and reaches a peak value of \(4.7 \times 10^{-11}\) mW m\(^{-1}\) K\(^{-2}\) when the conductivity is \(1.33 \times 10^2\) Scm\(^{-1}\). As the conductivity increases further, the power factor begins to diminish slowly. This power factor behavior implies that a conductivity of approximately \(1.33 \times 10^2\) Scm\(^{-1}\) leads to the optimal thermoelectric properties. Compared to other silicon-based materials such as silicon nanowires, the properties of the silicon MCPs are not significantly better. However, there is room for development for silicon MCPs and the microelectronic-compatible technology is favored by the industry. For instance, by changing the pore size and spacing, filling the pores fully or partially with other materials, doping with other elements besides boron, and reducing the surface states, the conductivity and thermoelectric properties of the silicon MCPs can be further enhanced [14,15].

4. Conclusion

Silicon MCPs were fabricated by PAECE and the electrical conductivity was modified by boron doping for different times. The doped samples possess enhanced electrical conductivity. However, the absolute Seebeck coefficient at room temperature decreases when the electrical conductivity increases and it shows the same trend as other semiconductors. The power factor based on the Seebeck coefficient and electrical conductivity reveals a maximum value of \(4.7 \times 10^{-11}\) mW m\(^{-1}\) K\(^{-2}\) at an electrical conductivity of \(1.33 \times 10^2\) Scm\(^{-1}\). Boron doping is thus a suitable method to enhance the thermoelectric property of silicon MCPs and the mature silicon technology renders boron-doped silicon MCPs attractive to power generation.

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