

## Enhancement of Thermoelectric Properties via Radial Dopant Inhomogeneity in B-doped Si Nanowires

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### Abstract

We demonstrate an enhancement of thermoelectric properties via a radial dopant inhomogeneity in B-doped Si nanowires. These nanowires were naturally composed of a heavily doped outer shell layer and a lightly doped inner core due to the occurrence of vapor-solid growth on the nanowire surface during vapor-liquid-solid (VLS) method. The thermopower measurements for a single nanowire demonstrated that the Seebeck coefficient value increased up to 1.8 times compared with homogeneously B-doped Si when the apparent nanowire resistivity was above  $10^{-2}$   $\Omega\text{cm}$ . The field effect measurements clarified that in such resistivity range the apparent hole mobility values of these nanowires were higher than those of homogeneously B-doped Si. This mobility enhancement lowers overall electrical resistivity of nanowires while without decreasing Seebeck coefficient value, resulting in the enhancement of thermoelectric power factor. In addition, we found that tailoring the surface dopant distribution by introducing surface  $\delta$ -doping can further increase the Seebeck coefficient value up to 2.2 times compared with homogeneous doped system.

### 1. Introduction

Thermoelectric power generation holds great promise for waste heat recovery. Intensive efforts have been devoted to improve the energy conversion efficiency of thermoelectric devices. The figure of merit  $ZT$  is well known to determine the conversion efficiency. However, due to the strong inter-correlation between these parameters, enhancing the  $ZT$  value has been limited in bulk materials. Decreasing the thermal conductivity via increasing the phonon scattering in nanostructures has been a traditional approach to improve the  $ZT$ . Among various nanostructures, self-assembled semiconductor nanowires hold great promise for improving the  $ZT$ . The well-known difficulty to increase the power factor in nanowires is due to the surface states, which reduces the mobility and conductivity via the surface trapping and scattering. One simple solution to overcome this issue is to create the mobile carriers far from the nanowire surface. Utilizing a core/shell structure might be the solution

to achieve this. Although intentionally controlling the radial dopant inhomogeneity might be a promising way to create such high mobility carriers even without the use of hetero-interfaces, the role of radial dopant inhomogeneity on thermoelectric properties of nanowires has not been clarified yet.

### 2. Results and Discussion

Figure 1a shows the measured Seebeck coefficient data for B-doped Si nanowires, whose electrical resistivity values were ranged from  $10^{-3}$  to  $10^2$   $\Omega\text{cm}$ . Although the nanowires were collected from the same sample, the resistivity values were widely distributed. Note that we intentionally utilized the resistivity distribution to examine the correlation between the Seebeck coefficient and electrical resistivity. For comparison, the reference data on B-doped Si (including bulk and nanowire) were shown in figure. As seen in figure, for relatively low resistivity range below  $10^{-2}$   $\Omega\text{cm}$ , both the nanowire and the reference values were ranged below 400  $\mu\text{V/K}$ . Above  $10^{-2}$   $\Omega\text{cm}$ , the Seebeck coefficient of nanowires tends to be significantly higher than the reference data. For the resistivity  $\sim 10^2$   $\Omega\text{cm}$ , the Seebeck coefficient value ( $\sim 1770$   $\mu\text{V/K}$ ) was nearly 1.8 times higher than the reference data ( $\sim 1000$   $\mu\text{V/K}$ ).

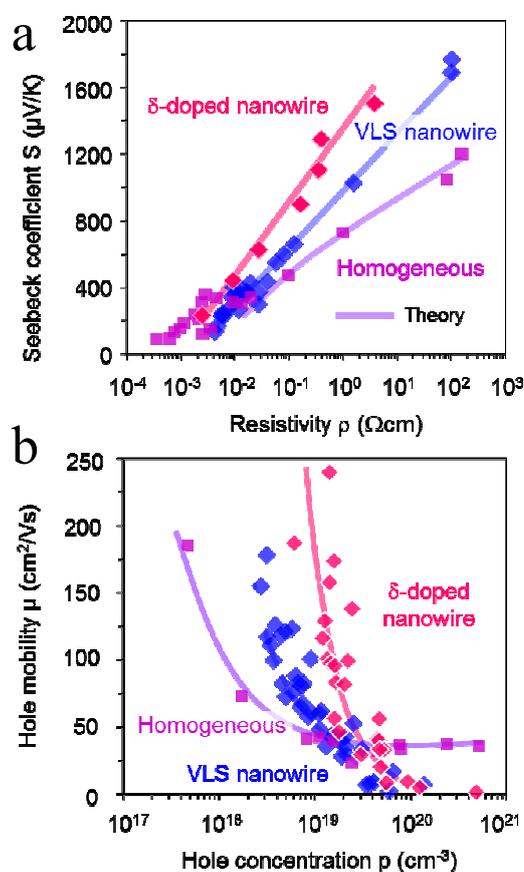
There are several possible scenarios to explain the observed enhancement of Seebeck coefficient in the present B-doped Si nanowires. The scenario is based on the presence of inhomogeneous dopant distribution within our B-doped Si nanowires grown by VLS process (*i.e.* heavily doped outer shell and the lightly doped inner core). In general, Seebeck coefficient value tends to be higher as the electrical conductivity decreases, as also seen in figure. If there is the difference between the heavily doped outer shell and the lightly doped inner core on the electrical conductivity due to the different dopant concentration, the variation of Seebeck coefficients should also exist along the radial direction of present nanowires. Thus, the combination of both core and shell properties, including the Seebeck coefficient and conductivity, determines the apparent physical properties of nanowires. In addition, the mobile carriers might diffuse from the heavily doped outer shell to the lightly doped inner core. If such diffused carriers exist in the lightly doped core, the apparent mobility of nan-

owires should be enhanced when compared with homogeneously doped systems due to the suppression of ionized impurity scattering.

To examine above scenario, the field effect measurements were performed to extract the mobility and the carrier concentration in our B-doped Si nanowires. The details of field effect measurements can be seen in the supporting information. Figure 1b shows the extracted hole mobility data plotted as a function of the apparent hole carrier concentrations within nanowires. Reference data of homogeneously B-doped Si are shown for comparison. As seen in the figure, the mobility data of the present B-doped Si nanowires were higher than the data of homogeneously B-doped Si when the carrier concentration was ranged below  $10^{19}$  cm<sup>-3</sup>. This carrier concentration range is in fact well consistent with the resistivity range  $\rho > 10^{-2}$   $\Omega$ cm in figure, where the Seebeck coefficient tends to deviate from the reference data. On the other hand, as shown in the inset, there was no significant difference between the present nanowires and homogeneously B-doped Si on the Seebeck coefficient data as a function of the carrier concentration. Since the mobility enhancement lowers overall electrical conductivity of nanowires while without reducing the Seebeck coefficient value, this effect apparently improves the thermoelectric properties of nanowires. Hence, these mobility data are consistent with the scenario based on the presence of inhomogeneous dopant radial distribution to explain the observed enhancement of Seebeck coefficient. Here we question the inherent nature of mobility enhancement when the radial dopant profile exists. The scenario is based on the difference between the inner core and the outer shell on the carrier scattering. If the gradient of B dopant concentration exists in the radial direction of the present nanowires (heavily doped outer shell/lightly doped inner core), the carrier diffusion from the outer shell to the inner core might occur, as supported by our electrostatic simulations in the supporting information. This might enhance the apparent mobility of nanowires when compared with homogeneously doped nanowires due to the decreased impurity scattering in the inner core.

Finally, we try to further enhance the role of heavily doped shell layer on the Seebeck coefficient values. In principle, the thinner doped shell layer with sharper dopant gradient should enhance the contribution of diffused carries from outer shell to inner core on the overall thermoelectric properties of nanowires. Thus we create such thinner doped shell layer by utilizing surface  $\delta$ -doping. The  $\delta$ -doped nanowires were formed by preparing a heavily B-doped shell layer on the intrinsic Si nanowires. Figure 1a shows the measured Seebeck coefficient data of  $\delta$ -doped Si nanowires. Interestingly, the Seebeck coefficient values of  $\delta$ -doped nanowires were further enhanced and higher than those of VLS grown B-doped Si nanowires when the resistivity was above  $10^{-2}$   $\Omega$ cm. For example, in the resistivity range  $\sim 1$   $\Omega$ cm, the Seebeck coefficient value of  $\delta$ -doped nanowires ( $\sim 1550$   $\mu$ V/K) was nearly 2.2 times higher than homogeneously B-doped Si data ( $\sim 700$   $\mu$ V/K). This further enhancement of Seebeck coefficient values via  $\delta$ -doping

highlights the critical role of heavily doped shell layer on the overall thermoelectric property of nanowires. Next, we examine the transport properties (mobility and carrier concentration) of  $\delta$ -doped Si nanowires by utilizing field effect measurements to reveal the role of  $\delta$ -doping on the Seebeck coefficient data. Figure 1b shows the extracted hole mobility data of  $\delta$ -doped nanowires as a function of the carrier concentration. The mobility values of  $\delta$ -doped Si nanowires were higher than those of VLS grown B-doped Si nanowires when the carrier concentration was below  $10^{19}$  cm<sup>-3</sup>. This carrier concentration range is consistent with the resistivity range  $\rho > 10^{-2}$   $\Omega$ cm. Thus, this further mobility enhancement, which lowers overall electrical resistivity without decreasing Seebeck coefficient values, increases apparently the Seebeck coefficient values of  $\delta$ -doped nanowires as a function of electrical resistivity.



**Figure 1** (a) Seebeck coefficient data for B-doped Si nanowires, (b) Hole mobility data of B-doped Si nanowires.

#### Acknowledgements

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#### References

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