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Semimetal–semiconductor transition in $Bi_{1-x}Sb_x$ alloy nanowires and their thermoelectric properties

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The resistivity of $Bi_{1-x}Sb_x$ nanowire arrays exhibits complex variations as a function of Sb content x and temperature T due to the unique semimetal-to-semiconductor (SM–SC) transition experienced by the nanowires. Seebeck coefficient measurements show enhanced thermopower due to Sb alloying and the reduction in wire diameter. The theoretical model not only explains these transport measurements, but also suggests a useful technique to experimentally determine (i) whether the wire is semimetallic or semiconducting, (ii) the carrier concentration, and (iii) the conditions for the SM–SC transition.
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The pursuit for different thermoelectric (TE) materials using low-dimensional systems has recently become an active research field,[1,2] since band structure[3,4] and phonon engineering[5,6] can be used to overcome the efficiency barriers imposed by the physics of conventional bulk materials. The TE efficiency is usually expressed by a dimensionless figure of merit: $ZT = S^2\sigma T/\kappa$, where S, σ, κ, and T are the Seebeck coefficient (or thermopower), electrical conductivity, thermal conductivity, and absolute temperature, respectively.

Theoretical calculations have predicted that bismuth (Bi) and its related alloys are promising candidates for low-dimensional TE materials at $\sim$100 K,[4,7] and that Bi nanowires (NWs) may possess ZT values of practical interest for wire diameters $d_W \leqslant 10$ nm.[4] Recent calculations further showed that by alloying Bi with Sb, desirable ZT values may be realized at $d_W \sim 40$ nm for $Bi_{1-x}Sb_x$ NWs.[8] In addition to their promise for TE applications, $Bi_{1-x}Sb_x$ NWs also constitute an attractive model system to study the transport behavior in low-dimensional structures due to their tunable band structures,[9] small electron effective masses, and long carrier mean free paths. However, some of the essential characterization parameters, such as the carrier density and resistivity, are found to be difficult to measure in NWs because of the lack of conventional techniques (e.g., Hall measurements) and the manifestation of unfavorable material attributes on the nanometer scale.[10] Therefore, one of the goals of this letter is to develop a strategy to determine these important quantities and to identify signatures of band structure variations by utilizing model calculations in conjunction with available experimental results.

In this letter, we report results of transport measurements on $Bi_{1-x}Sb_x$ nanowire (NW) arrays with $d_W \leqslant 100$ nm. The resistivity of 65 nm $Bi_{1-x}Sb_x$ NWs shows complex variations as a function of x and T, exhibiting features related to the *semimetal-to-semiconductor* (SM–SC) transition previously observed in Bi NW systems.[11,12] The transport model we have developed not only explains the complex $R(T)$ behavior, but also suggests an approach to experimentally determine the condition for the SM–SC transition. Seebeck coefficient (S) measurements show enhancement in the thermopower due to Sb alloying and the reduction in d_w. Based on the same transport model, we estimate the carrier concentration n contributed by uncontrolled impurities to be between 1×10^{16} and 4×10^{16} cm^{-3}, consistent with values reported previously.[12,13] The use of the S measurement as a means to determine n and whether the NW is semimetallic or semiconducting is also discussed.

$Bi_{1-x}Sb_x$ NW arrays in this study were prepared by pressure injecting molten $Bi_{1-x}Sb_x$ alloys into the pores of anodic alumina templates.[14] The Sb concentration in the alloy NWs was quantified by energy dispersive spectroscopy analysis on a single nanowire. The obtained Bi/Sb ratio in the NW was consistent with the alloy used, and the composition variation was within the measurement error range. Resistance measurements were performed for $2 \leqslant T \leqslant 300$ K, and the results are shown in Fig. 1 for 65 nm $Bi_{1-x}Sb_x$ NW arrays. In Fig. 1, the measured resistance R of pure Bi NWs exhibits a nonmonotonic T dependence with a maximum at $\sim$70 K, while $R(T)$ of the two alloy NW samples (with 5 and 10 at. % Sb) decreases with increasing T. In addition, $R(T)$ of the $Bi_{0.95}Sb_{0.05}$ NWs displays a stronger T dependence than that of the $Bi_{0.90}Sb_{0.10}$ NWs. This non-monotonic shift in the T dependence of the $R(T)$ as a function of x is strikingly similar to the previously measured $R(T)$ results of pure Bi NWs of different d_w.[11,12] It was found that while $R(T)$ of larger-d_w (200 and 70 nm) Bi NWs shows a nonmonotonic T dependence, that of smaller-d_w ($\leqslant$48 nm) Bi nanowires decreases monotonically with increasing T, and their dependence on T weakens as d_W decreases. The resemblance in the two sets of experimental findings suggests that in Bi NWs, the alloying with Sb and the reduction of d_w may have common effects on the band structure and transport properties, i.e., the SM–SC transition.[4] Although both bulk Bi and Sb are semimetals, bulk $Bi_{1-x}Sb_x$ alloys become semiconducting for $0.07 \leqslant x \leqslant 0.22$.[9] In $Bi_{1-x}Sb_x$ NWs, the

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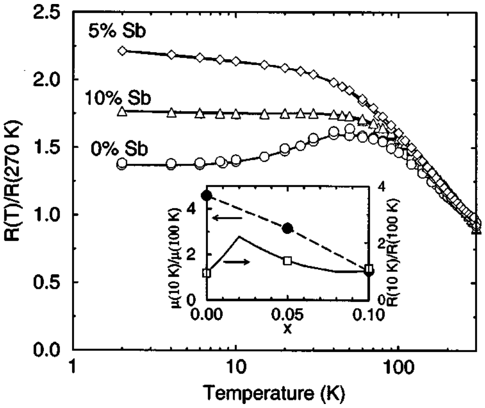

FIG. 1. Measured T dependence of the 270 K normalized resistance of 65 nm $Bi_{1-x}Sb_x$ nanowires with different Sb contents. The inset shows ratios of the mobility $\mu(10\ \mathrm{K})/\mu(100)$ K for the three samples (●) and the predicted $R(10\ \mathrm{K})/R(100\ \mathrm{K})$ (□) as a function of x.

x range for the semiconducting phase is broadened due to the quantum confinement effect. Rabin *et al.*[8] predicted a semiconducting phase for 65 nm $Bi_{1-x}Sb_x$ NWs of $0.03 \leqslant x \leqslant 0.27$, with the maximal gap E_g at $x \sim 0.15$.

Calculations have also predicted the SM–SC transition in Bi nanowires due to quantum confinement for $d_W \leqslant 50$ nm,[4] and an increase in the band gap E_g with decreasing d_w. Therefore, both Fig. 1 and the previous results[12] indicate that in Bi-related NWs, semiconducting wires possess a monotonically decreasing $R(T)$ with increasing T, while semimetallic NWs exhibit a maximum normalized resistance below 100 K, consistent with theoretical predictions.[12] The weakened T dependence for semiconducting wires with increasing E_g is explained below. The agreement between theoretical predictions and these two sets of experiments not only provides strong evidence for the SM–SC transition in Bi-related NWs, but also validates our transport model for nanowires.

We note that in Fig. 1, the temperature-dependent resistivity $\rho(T)$ of semiconducting wires (with 5 and 10 at. % Sb) saturates at low T instead of exhibiting a T dependence of $\exp(E_g/2kT)$, characteristic for semiconductors. This $\rho(T)$ saturation was also observed in semiconducting Bi NWs,[11,12] and it was attributed to uncontrolled impurities introduced during nanowire synthesis. The uncontrolled impurity density, estimated[12] to be $\sim 10^{16}\ \mathrm{cm}^{-3}$, has little effect for semimetallic wires that usually have an intrinsic carrier density $>10^{17}\ \mathrm{cm}^{-3}$. However, for semiconducting wires with a larger E_g, the extrinsic carriers that have a T-independent carrier concentration will dominate over thermally excited carriers over a broader temperature range as T increases, resulting in a weaker T dependence of $\rho(T)$, as observed experimentally.

Assuming an extrinsic impurity carrier concentration of $4\times 10^{16}\ \mathrm{cm}^{-3}$, we calculated the total carrier concentration of the 65 nm $Bi_{1-x}Sb_x$ NWs below 100 K. The band structure above 100 K becomes highly T dependent[15] and the parameters are not well established. The ratios of the total carrier concentration $n(100\ \mathrm{K})/n(10\ \mathrm{K})$ are calculated as 4.2, 4.3, and 1.4 for nanowires with 0, 5, and 10 at. % Sb, respectively. Based on the calculated n and measured resistance, the average mobility ratio $\mu(10\ \mathrm{K})/\mu(100\ \mathrm{K})$ is obtained for the three samples, as shown by the dashed curve in the inset of Fig. 1. Although the measured $R(10\ \mathrm{K})/R(100\ \mathrm{K})$ shows complex variations as a function of x, the mobility ratio of 65 nm NWs decreases monotonically as x increases, indicating that μ becomes less T dependent as x increases due to increased neutral impurity scattering. Assuming a linear dependence to interpolate the mobility ratio for $0.0 \leqslant x \leqslant 0.1$, we calculate $R(10\ \mathrm{K})/R(100\ \mathrm{K})$ for 65 nm $Bi_{1-x}Sb_x$ NWs as a function of x (see inset of Fig. 1). As x increases, this resistance ratio of semimetallic wires rises due to the decreased conduction–valence band overlap. In contrast, the resistance ratio decreases for semiconducting wires due to the increasing dominance of extrinsic carriers. The maximum in $R(10\ \mathrm{K})/R(100\ \mathrm{K})$ at $x \sim 0.02$ corresponds to the Sb content for the predicted SM–SC transition. Thus, by examining the resistance ratios of Bi and $Bi_{1-x}Sb_x$ NWs as a function of d_w and x, we can identify experimentally the actual wire diameter and Sb content at which the SM–SC transition occurs.

The Seebeck coefficient measurements are essential for evaluating the performance of TE materials. Since the S measurement is intrinsically independent of the number of nanowires contributing to the signal, the measurements on NW arrays are in theory as informative as single-wire measurements. However, there has been limited progress in S measurements of NW arrays until recently.[16] The experimental setup for the S measurement of NW arrays is described in Ref. 17. Figure 2 shows the measured $S(T)$ for bulk Bi and for NW arrays with different d_w and x. The measured S of the bulk Bi sample is about $-45\ \mu\mathrm{V/K}$ at 300 K, which is in good agreement with literature values, as well as with its T dependence $\partial S/\partial T$.[18] The measured S of 65 nm and 40 nm Bi nanowires at 300 K are -48 and $-55\ \mu\mathrm{V/K}$, respectively. Although the measured S of NW arrays is usually underestimated, the enhancement of S in NW arrays is encouraging and important in validating the experimental techniques used.

Figure 2 shows that the Seebeck coefficient of ~ 40 nm NWs is slightly larger in magnitude than that of 65 nm NWs for both Bi and $Bi_{0.95}Sb_{0.05}$ over the T range measured, which may be due to a sharper density of states and a smaller band overlap as d_w decreases.[4] For Bi NWs alloyed with 5 at. % Sb, we note some increase in $|S|$ over pure Bi NWs for both diameters (~ 40 and 65 nm), with the smaller diameter NWs showing a more significant enhancement. These results indicate that Sb alloying and the confinement effects in Bi are both effective at decreasing the band overlap and enhancing the thermopower.

From the measured $S(T)$ and model calculations, we can extract valuable information, such as the Fermi energy and the carrier concentration n. Based on the transport model for $Bi_{1-x}Sb_x$ NWs developed in Ref. 8, Figure 3 shows the calculated $|S|$ as a function of d_w for Bi and $Bi_{0.95}Sb_{0.95}$ NWs at three different n-type dopant concentrations (1×10^{16}, 2×10^{16} and $4\times 10^{16}\ \mathrm{cm}^{-3}$) at 100 K. Also shown in Fig. 3 are the corresponding measured S data for Bi (●) and $Bi_{0.95}Sb_{0.05}$ (△) NWs at 100 K. Good agreement between the experimental results and the theoretical model is obtained, and the corresponding dopant carrier concentrations ($\sim 1\times 10^{16}$ to $4\times 10^{16}\ \mathrm{cm}^{-3}$) also agree with the uncontrolled

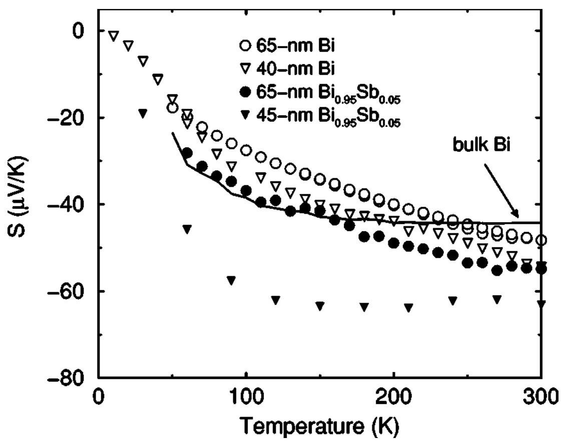

FIG. 2. Measured Seebeck coefficient as a function of T for Bi (○, ▽) and $Bi_{0.95}Sb_{0.05}$ (●, ▼) nanowires with different diameters. The solid curve denotes the Seebeck coefficient for bulk Bi.

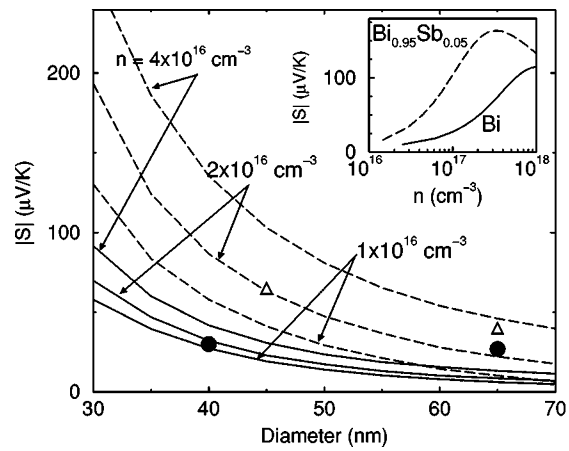

FIG. 3. The theoretically predicted magnitude of the Seebeck coefficient as a function of d_W at 100 K for Bi (solid curve) and $Bi_{0.95}Sb_{0.05}$ (dashed curve) nanowires at different dopant concentrations. Also shown are measured $|S|$ of Bi (●) and $Bi_{0.95}Sb_{0.05}$ (△) nanowires at 100 K. The inset shows the calculated $|S|$ as a function of carrier concentration at 100 K for 65 nm Bi (solid curve) and $Bi_{0.95}Sb_{0.05}$ (dashed curve) nanowires.

impurity carrier concentrations derived from other experiments.[12,13] The inset in Fig. 3 shows the calculated $|S|$ as a function of carrier concentration n for 65 nm Bi and $Bi_{0.95}Sb_{0.05}$ NWs. We note that $|S|$ is much more sensitive to n in semiconducting NWs (e.g., $Bi_{0.95}Sb_{0.05}$) than in semimetallic NWs, because the Fermi level has a stronger dependence on n for semiconducting wires. This result has important implications that may be useful for characterizing NWs. First, from the change in S as a function of n, we may distinguish semiconducting from semimetallic NWs. In addition, the strong dependence of S on n for semiconducting NWs renders the S measurement a promising probe to determine the carrier concentration in NWs. From Fig. 3, it is also expected that a higher S can be achieved at higher n ($>10^{17}\ \mathrm{cm}^{-3}$) by intentionally doping the NWs with electron donors (e.g., Te).

In summary, we present here resistance and Seebeck coefficient measurements of $Bi_{1-x}Sb_x$ NW arrays which are explained by our theoretical model. We observe a complex behavior in $R(T)/R(270\ \mathrm{K})$ of 65 nm $Bi_{1-x}Sb_x$ NWs as a function of x and T which provides a signature of the SM–SC transition in Bi-based systems. Model calculations also suggest an approach to determine the conditions for this SM–SC transition via $R(T)$ measurements. Nanowire arrays exhibit an enhanced thermopower as the d_w decreases and as a result of Sb alloying, and demonstrate enhanced thermoelectric properties in 1D NW systems. The carrier concentration contributed by uncontrolled impurities in these NWs is estimated to be between 1×10^{16} and $4\times10^{16}\ \mathrm{cm}^{-3}$. The S measurements, in conjunction with calculations, may provide a useful technique for determining the carrier concentration and whether the nanowire is semiconducting or semimetallic.

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